

2

SOLID STATE PHYSICS

Introduction

Matter exists in three states namely solids, liquids and gases. As the atoms or molecules in solids are attached to one another with strong forces of attraction, the solids have definite volume and shape. In this unit we shall deal with physical properties of solids, particularly crystals hence called solid state physics or crystal physics. The solids may be broadly classified as crystalline and non-crystalline (amorphous).

The crystalline state of a solid is characterised by regular or periodic arrangement of atoms or molecules. The crystalline solids may be subdivided into single crystals and polycrystalline solids. In single crystals, the periodicity of atoms extends throughout the material. Diamond, quartz, mica, etc. are examples of single crystals. A polycrystalline material is an aggregate of a number of small crystallites with random orientations separated by well defined boundaries. The small crystallites are known as grains and the boundaries as grain boundaries. Polycrystalline form of a material is more stable than a single crystal. Metals and ceramics exhibit polycrystalline structure.

Amorphous solids are characterised by the random arrangement of atoms or molecules. The periodicity, if at all present, extends up to a distance of a few atomic

Table 2.1 : Distinction between crystalline and amorphous solids

Crystalline	Amorphous
<ol style="list-style-type: none">1. The atoms or molecules are arranged in definite geometrical order giving definite geometrical pattern.2. The atoms are arranged in long range order.3. They have sharp melting point.4. They are anisotropic. Their physical properties like electrical conductivity, refractive index, thermal conductivity etc. are different along different directions.	<ol style="list-style-type: none">1. They do not possess definite geometrical pattern.2. The atoms are arranged in short range order.3. They do not have sharp melting point.4. They are isotropic. Their thermal conductivity, electrical conductivity, refractive index etc. are same in different directions.

diameters only. In other words; these solids exhibit short range order. Glass, plastics, rubbers, cement, paraffin wax etc. are amorphous solids.

The science which deals with the study of geometrical forms and physical properties of crystalline solids is called crystallography. This forms the basis to the study of solid state physics.

Lattice points and space lattice

The atomic arrangements in a crystal is called a crystal structure. In a perfect crystal, there is a regular arrangement of atoms. This periodicity in the arrangement generally varies in different directions. To describe a crystal structure we have to develop a geometrical artifice. For this imagine a large number of points in space about which the atoms are located. Such points in space are called lattice points and the totality of such points forms a space lattice (crystal lattice). The arrangement of infinite number of imaginary points in three dimensional space with each point having identical surroundings is known as space lattice.

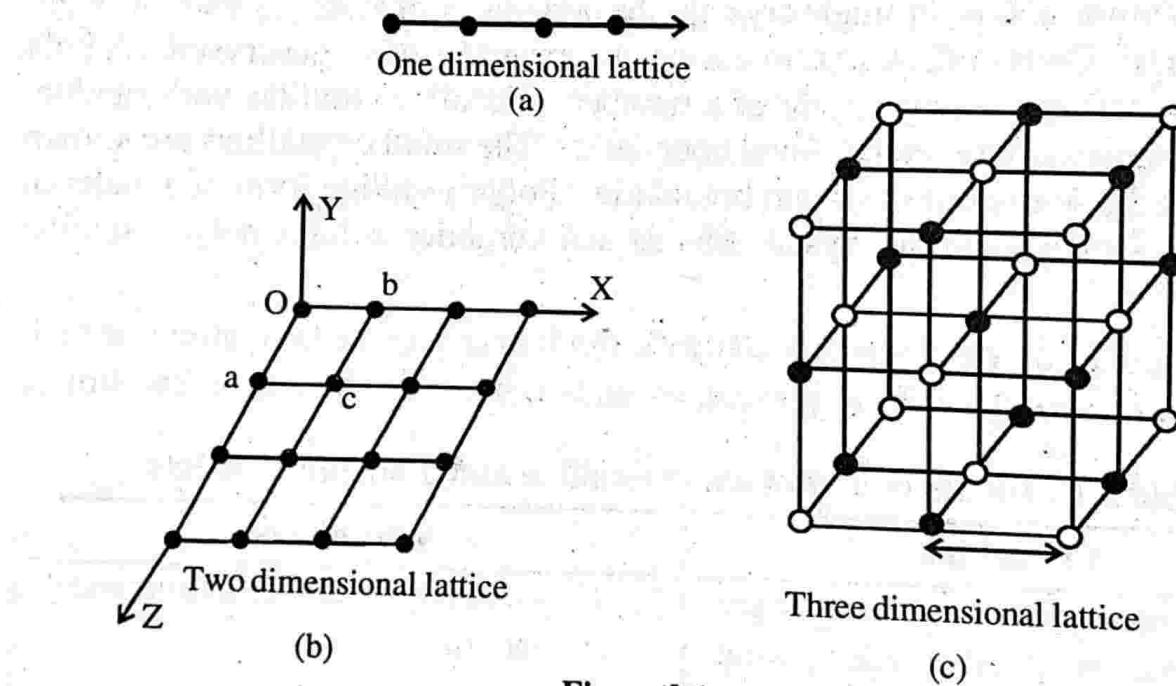


Figure 2.1

Remember that crystal lattice is purely an imaginary geometrical construction. In the definition of crystal lattice the term identical surroundings means that the lattice has the same appearance when viewed from a point \vec{r} in the lattice as it has when viewed from any other point \vec{r}' with respect to some arbitrary origin.

Let us consider the case of a two dimensional array of lattice points as shown below. It represents a space lattice since the environment about any two points is the same.

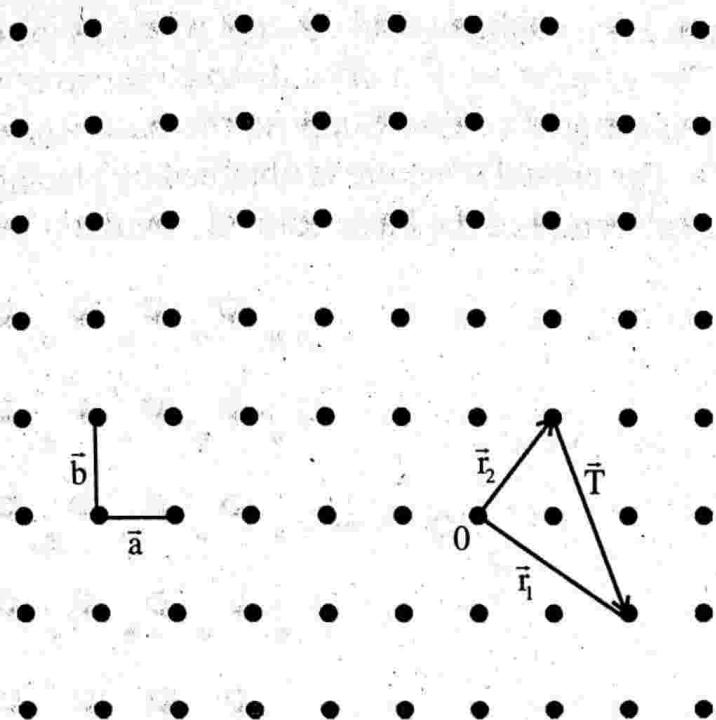


Figure 2.2

We choose an arbitrary origin 0 and position vectors \vec{r}_1 and \vec{r}_2 of any two lattice points by joining them to 0 as shown. If the difference \vec{T} of the two vectors \vec{r}_1 and \vec{r}_2 satisfies the relation.

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b}$$

where n_1 and n_2 are integers and \vec{a} and \vec{b} are fundamental translation vectors characteristic of the array, then the array of points is a two dimensional lattice.

For three dimensional lattice

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}.$$

The basis and crystal structure

The space lattice has been defined as an array of imaginary points which are so arranged in space that each point has identical surroundings. The crystal structure is always described in terms of atoms rather than points. Thus in order to obtain a crystal structure, an atom or a group of atoms must be placed on each lattice point in a regular fashion. Such an atom or a group of atoms is called the basis and acts as a building unit or a structural unit for the complete crystal structure. Thus a lattice combined with a basis generates the crystal structure. Mathematically it is expressed as

$$\text{Space lattice} + \text{basis} = \text{crystal structure}$$

Remember that lattice is a mathematical concept whereas the crystal structure is a physical concept. The generation of a crystal structure from a two dimensional lattice and a basis is illustrated below. Suppose the basis consists of two atoms represented by \circ and \bullet . The crystal structure is obtained by placing the basis on each lattice point such that the centre of the basis coincides with the lattice point.

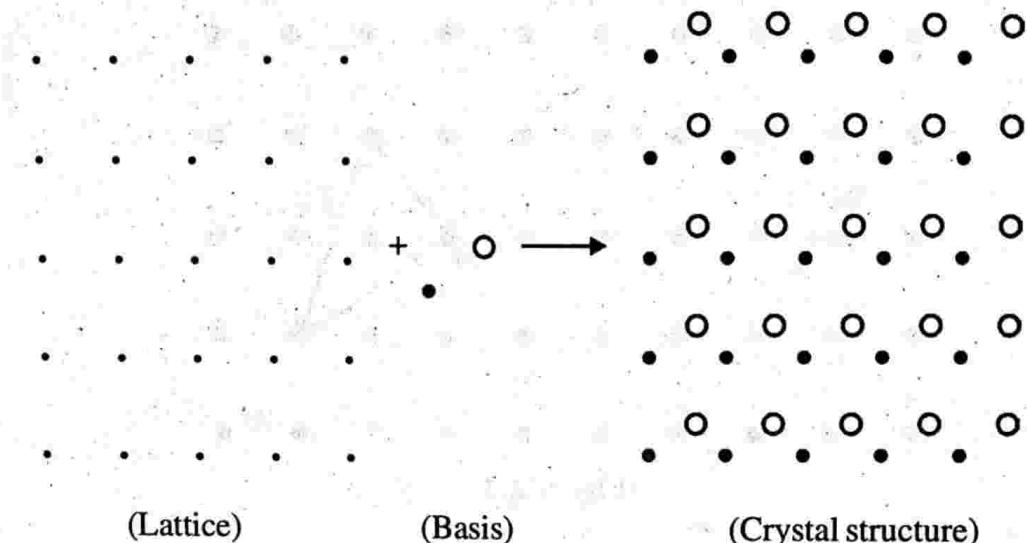


Figure 2.3

The number of atoms in a basis may vary from one to several thousands, whereas the number of space lattices possible is only fourteen. It shows that different types of basis are available. If the basis consists of a single atom only a mono atomic crystal is obtained. Copper is an example of mono atomic face centred cubic structures.

Unit cells and lattice parameters

A crystal structure is formed by the addition of basis to every lattice point. In describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called unit cells. i.e., in every crystal some fundamental grouping of particles is repeated. Such fundamental grouping of particles is called a unit cell.

A unit cell is chosen to represent the symmetry of the crystal structure, where in all the atom positions in the crystal may be generated by translations of the unit cell through distances along each of its edges. Thus, unit cell is the basic building block of the crystal structure by virtue of its geometry and atomic positions within the crystal. A unit cell or more than a single unit cell may be chosen to build up a crystal structure. Unit cells also may be regarded as the building blocks that make up the crystal.

Figure below shows a unit cell and the crystal formed with the help of such unit cells.

From the figure below we can have

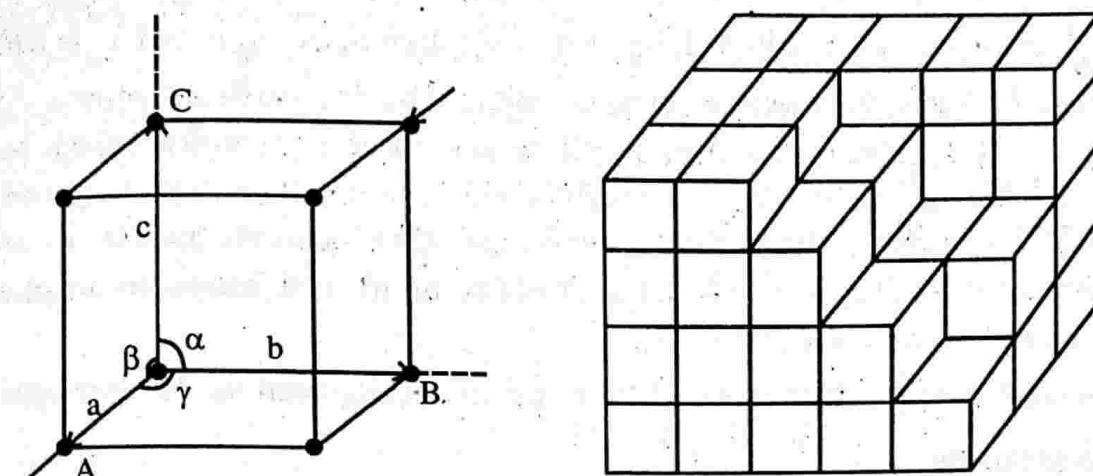


Figure 2.4

1. The line OA, OB and OC are obtained by the intersection of the adjacent faces of the unit cell. The directions parallel to these lines are called crystallographic axes.
2. The lengths of the sides OA = a, OB = b and OC = c are called lattice constants or primitives.
3. The angles α , β and γ between the crystallographic axes are called interfacial angles.

The above discussion shows that a unit cell can be completely described by the three vectors \vec{a} , \vec{b} and \vec{c} and angles between them (α , β , γ) are specified. \vec{a} , \vec{b} and \vec{c} are called lattice vectors. The lattice vectors \vec{a} , \vec{b} and \vec{c} and the interfacial angles constitute the lattice parameters of the unit cell. By knowing the lattice parameters we can easily determine the form and size of the unit cell.

It may also be noted that unit cells for most of the crystals are parallelepiped or cubes having three sets of parallel faces.

The lattice vectors \vec{a} , \vec{b} and \vec{c} may or may not be equal. Also the angles α , β and γ may or may not be right angles. Based on these conditions, there are seven different unit cells so also crystals. If atoms are existing at the corners of the unit cells, the seven unit cells yield seven crystal structures which gives seven types of lattices. More space lattices can be constructed by placing atoms at the body centres of unit cells or at the centres of faces. So we can have 14 different types of space lattices. These 14 space lattices are called Bravais lattice. Bravais is the name of the person who discovered this.

Unit cell versus primitive cell

The parallelepiped (or cube) defined by primitive axes \vec{a} , \vec{b} and \vec{c} is called a primitive cell. A primitive cell is a type of unit cell having smallest volume. All the lattice points belonging to a primitive cell lie at its corners. Therefore, the effective number of lattice points in a primitive cell is one. A unit cell on the other hand may have the lattice points at the corners as well as at other locations both inside and on the surface of the cell and therefore the effective number of lattice points in a non-primitive cell is greater than one.

A unit cells may be primitive cells but primitive cells need not be unit cells.

Crystal systems

Crystals have internal structure. Depending on their internal structures they exhibit symmetries. Based on the symmetries exhibited by crystals they are classified into 32 classes. Among the 32 classes of crystal systems there are only seven basic crystal structures. These seven basic crystal systems are distinguished from one another by the angles between the three axes (α , β and γ) and the lattice vectors (\vec{a} , \vec{b} and \vec{c}). They are 1. Cubic crystal 2. Tetragonal crystal 3. Orthorhombic crystal 4. Monoclinic crystal 5. Triclinic crystal 6. Triagonal crystal and 7. Hexagonal crystal.

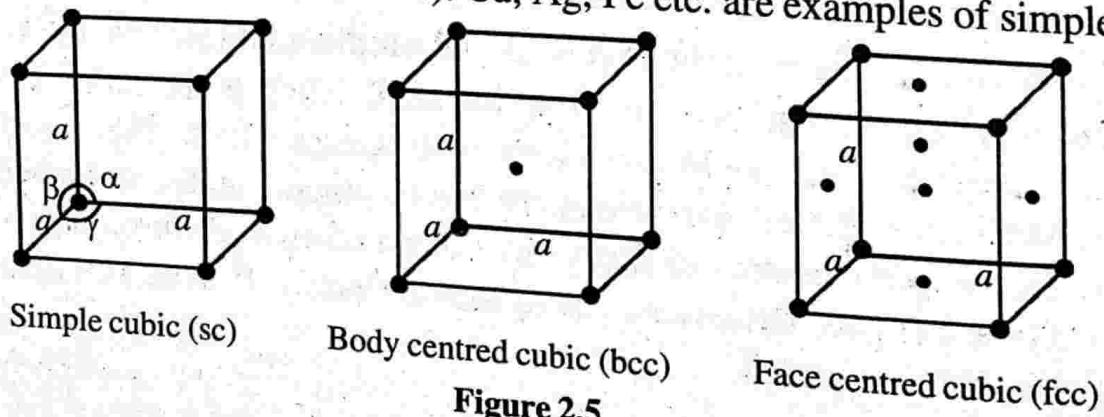
1. Cubic crystal system

In a cubic crystal the crystal axes are perpendicular to one another and the length of the lattice vectors are the same.

i.e., $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$

Cubic crystal may be simple cubic (sc), body centred cubic (bcc) or face centred cubic (fcc).

In the unit cell of simple cubic crystal structure the atoms are located at the corners only (each atom at each corner). Cu, Ag, Fe etc. are examples of simple cubic.

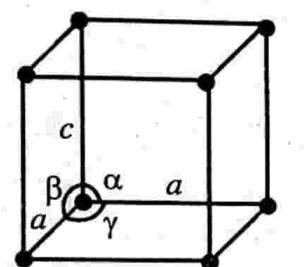


In the unit cell of body centred cubic crystal structure there are atoms located at the corners (each atom at each corner) and another atom at the body centre. Li, Na, K and Cr exhibit this structure. In the unit cell of face centred cubic (fcc) crystal structure, there are atoms located at the corners (each one at each corner) and each atom at the centres of six faces. NaCl, is an example for fcc.

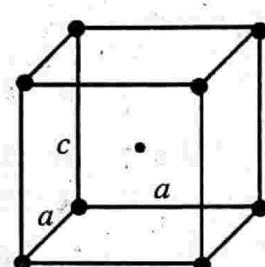
2. Tetragonal crystal system

Here $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$

i.e., The crystal axes are perpendicular and the length of two lattice vectors are the same but the length of the third lattice is different. Tetragonal crystal may be simple or body centred. β -Sn is an example for simple tetragonal and TiO_2 is an example for body centred tetragonal.



Simple tetragonal (st)



Body-centred tetragonal (bct)

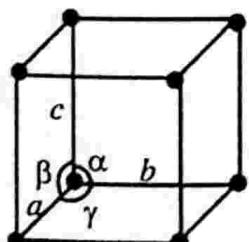
Figure 2.6

3. Orthorhombic crystal system

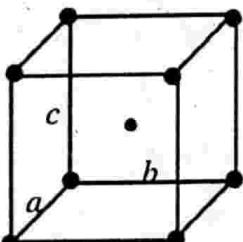
$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$

The crystal axes are perpendicular to one another but the length of the lattice vectors are different all along the three axes.

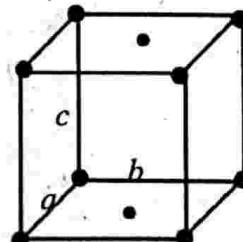
Orthorhombic crystals may be simple, base centred (end centred), body centred or face centred.



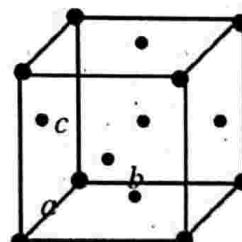
Simple orthorhombic



Body-centred orthorhombic



End centred orthorhombic



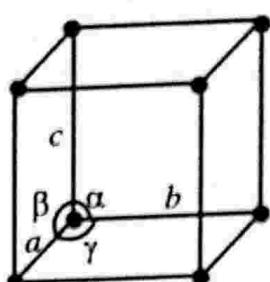
Face centred orthorhombic

Figure 2.7

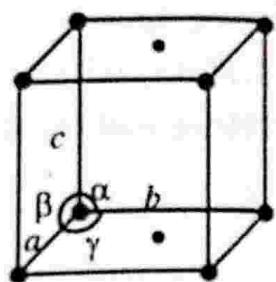
4. Monoclinic crystal system

$$a \neq b \neq c, \alpha = \beta = 90^\circ \neq \gamma$$

Here two of the crystal axes are perpendicular to each other but third axis is obliquely inclined. The length of the lattice vectors are different along all the three axes. Monoclinic crystals may be simple or base centred (end centred). $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) is an example for simple monoclinic.



Simple monoclinic



Base-centred monoclinic

Figure 2.8

5. Triclinic crystal system

$$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$$

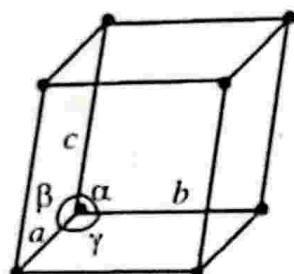
None of the crystal axes are perpendicular to any of the others and all the length of the lattice vectors are different. There is only simple triclinic crystal structure. $\text{K}_2\text{Cr}_2\text{O}_7$ is an example for this.

6. Trigonal (rhombohedral) crystal system

$$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$$

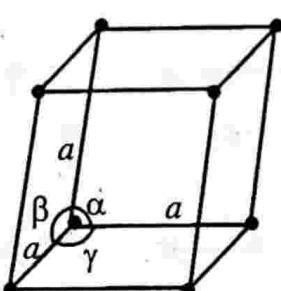
The length of the lattice vectors are equal and are equally inclined to each other at an angle other than 90° .

There is only simple trigonal crystal structure. As, Sb, Bi etc. exhibit this structure.



Simple triclinic

Figure 2.9



Simple rhombohedral

Figure 2.10

7. Hexagonal crystal system

$$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$$

Lengths of two lattice vectors are same but the length of third axis is different. Two of the crystal axes are 60° apart while the third is perpendicular to both of them. There is only simple hexagonal crystal structure. Mg, Zn, Cd etc. exhibit this structure.

The seven basic crystal structures and their properties are given in the table below.

Table 2.2 : Seven basic crystal systems and their characteristics

Sl. No.	Crystal system (7)	Lattice parameters	Bravais lattice (14)	Examples
1	Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	sc, bcc, and fcc	Ag, Cu, Fe
2	Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	st, bct	Li, Na, K, Cr, NaCl
3	Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	so, bco, eco, fco	$\beta\text{-Sn}, \text{TiO}_2$ $\text{KNO}_3, \text{BaSO}_4$ PbCO_3
4	Monoclinic	$a \neq b \neq c, \alpha = \beta = 90^\circ \neq \gamma$	sm, ecm	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{FeSO}_4, \text{Na}_2\text{SO}_4$
5	Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	st	$\text{K}_2\text{Cr}_2\text{O}_7, \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
6	Trigonal	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	sr	As, Sb, Bi, Calcite
7	Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	sh	$\text{SiO}_2, \text{Zn}, \text{Mg}, \text{Cd}$.

Crystal symmetry

All crystals have ordered arrangements of the faces and edges. i.e., we can say that crystals possess symmetries. We know that symmetry plays an important role in dictating the dynamics and properties of a system. Here the symmetry possessed by crystals acts as a powerful tool for the study of the internal structure of crystals. From this we can extract the properties of solids which are constructed from the basic crystal structures.

The symmetries possessed by crystals are described in terms of symmetry operations. A symmetry operation is that which transforms the crystals to itself. i.e., a

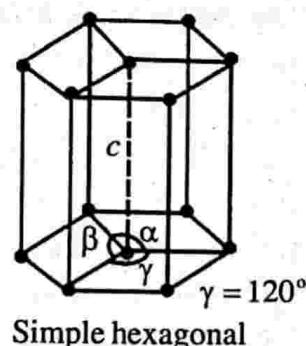


Figure 2.11

crystal remains invariant under a symmetry operation. These operations are translation, rotation, reflection and inversion. The last three operations are point operations and their combinations give certain symmetry elements which collectively determine the symmetry of crystal around a point. The group of such symmetry operations at a point is called a point group. There are totally 32 point groups in a 3D lattice. The group of all the symmetry elements of a crystal structure is called a space group (point group symmetry operations combined with translational symmetry elements). There are totally 230 distinct space groups in 3D lattice exhibited by crystals.

The 32 point groups in 3D produce only 14 distinct Bravais lattices. These 14 Bravais lattices can be constructed from 7 distinct crystal systems which we already explained.

The 23 symmetry elements in a cubic crystal

Here we discuss about the point symmetries exhibited by a cubic crystal. We could already see that there are three symmetries come under this. They are 1) inversion 2) reflection and 3) rotation.

Inversion symmetry of a cubic crystal

Inversion is a point operation which is applicable to 3-dimensional lattices only. This symmetry element implies that each point located at \vec{r} relative to a lattice point has an identical point located at $-\vec{r}$ relative to the same lattice point. In other words it means that the lattice possesses a centre of inversion or centre of symmetry. Consider a cubic crystal. It has three pairs of parallel and opposite faces all of them of the same size and shape. Here the body centre is a centre of symmetry. This centre lies at equal distances from various symmetrical positions. Here for every lattice point given by the position vector \vec{r} there is a corresponding lattice point at the position $-\vec{r}$. Hence we can say that cube possesses a centre of symmetry.

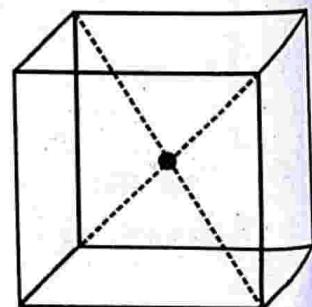


Figure 2.12

2. Reflection symmetry of a cubic crystal (plane of symmetry)

A lattice is said to possess reflection symmetry if there exists a plane (or a line in two dimensions) in the lattice which divides it into two identical halves which are mirror images of each other. In other words a crystal is said to possess reflection symmetry about a plane if it is left unchanged in every way after being reflected by the plane.

In a cubic crystal we can see there are three straight planes of symmetry parallel to the faces of the cube and six diagonal planes of symmetry (see figure below).

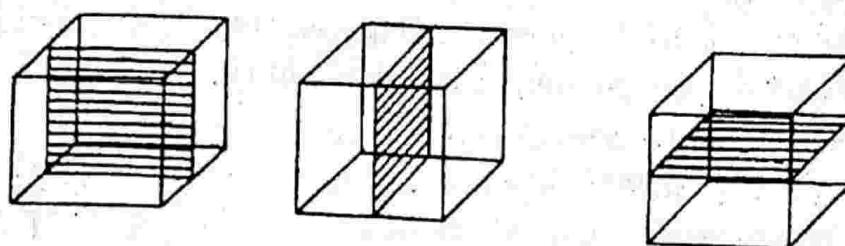


Figure 2.13 : The three planes of symmetry parallel to the faces of the cube

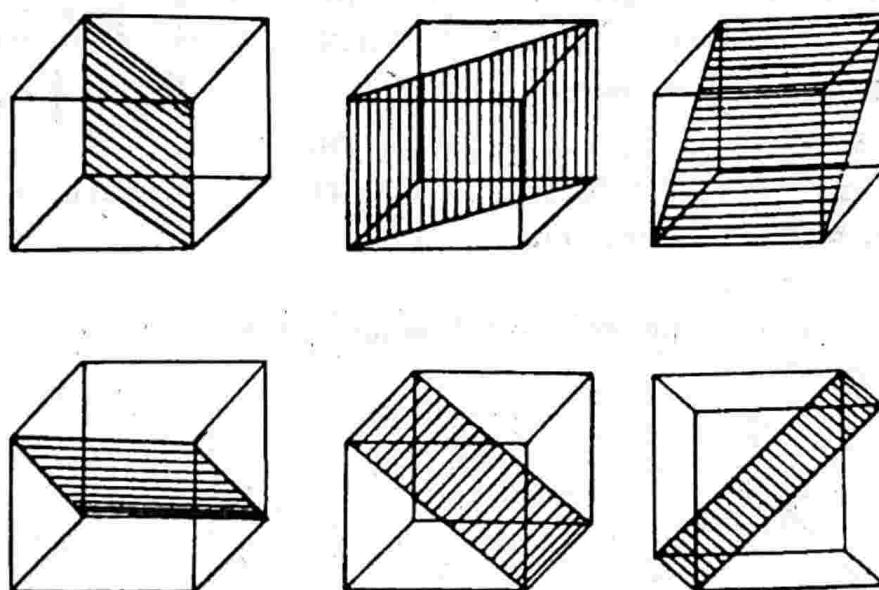


Figure 2.14: The six diagonal planes of symmetry in a cube

Note: Reflection occurs in a plane through the lattice point, while the inversion is equivalent to a reflection through a point.

Rotation symmetry of a cubic crystal

A lattice is said to possess the rotation symmetry if its rotation by an angle θ about an axis (or a point in a two dimensional lattice) transforms the lattice to itself. Since the lattice always remains invariant by a rotation of 2π , the angle 2π must be an integral multiple of θ .

$$\text{i.e., } n\theta = 2\pi$$

$$\text{or } \theta = \frac{2\pi}{n}$$

The factor n takes integral values and is known as multiplicity of rotation axis. The value of n decides the fold of the axis. Only one, two, three, four and six fold rotation axes of symmetry are possible in a crystal lattice.

If a cube is rotated about a normal to one of its faces at its mid point through 90° , cube is indistinguishable from the position it occupied originally.

Thus the normal is an axis of 4 fold $\left(\frac{360}{90}\right)$ symmetry.

Hence it is called a tetrad axis. A cube possesses three such axes, one normal to each of the three pairs of parallel faces. (see figure below)

The three tetrad axis of a cube. If a cube is rotated about a body diagonal through 120° , the cube will remain invariant. Then the body diagonal is a

triaid $\left(\frac{360}{120} = 3\right)$ axes. A cube possesses four such axes.

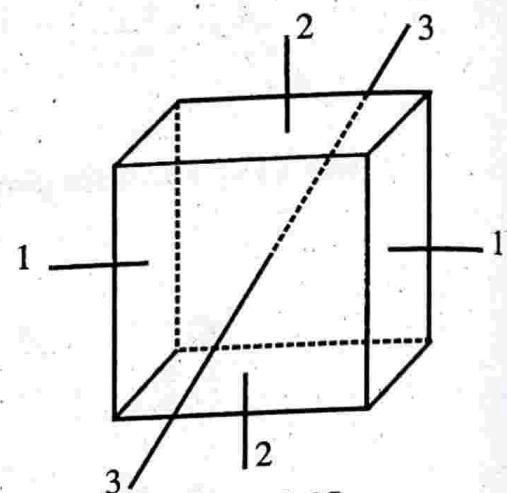
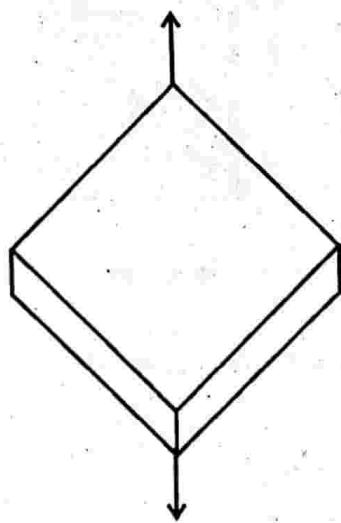
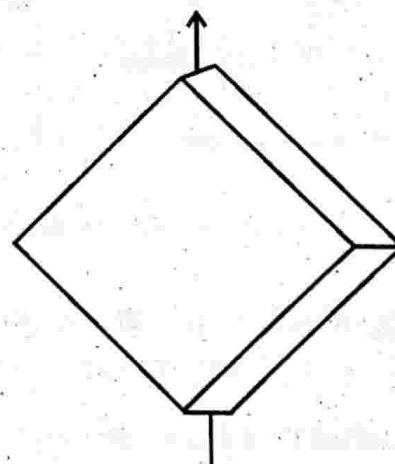


Figure 2.15



One of the triad axes of the cube



One of the diad axes of the cube

Figure 2.16

If a cube is rotated about a line joining the mid points of a pair of opposite parallel edges through 180° , the cube is indistinguishable from the position it occupied originally.

Thus the line is an axis of two $\left(\frac{360}{180} = 2\right)$ fold symmetry. Hence it is called a diad axis. A cube possesses six such axes.

To sum up, the various symmetry elements in a cubic crystal are

Inversion symmetry – 1

Reflection symmetry

Straight planes – 3

diagonal planes – 6

tetrad axes – 3

triad axes – 4

diad axes – 6

∴ Total symmetry elements of a cubic crystal is 23.

Rotation - inversion axis

A crystal is said to possess a rotation - inversion axis if it is brought back to its original condition by rotation followed by an inversion about a lattice point through which the rotation axis passes.

Let us consider an axis normal to the circle passing through the centre, operating on a pole 1 to rotate it through 90° anticlockwise to the position 4, followed by an inversion to the position 2. From the position 2 the pole is rotated through 90° anticlockwise and inverted to position 3. From position 3 it is further rotated through 90° anticlockwise and inverted to position 4. Further 90° rotation and an inversion the pole resumes position 1. Crystals can possess 1 –, 2 –, 3 –, 4 – and 6 – fold rotation inversion axes, represented by $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$.

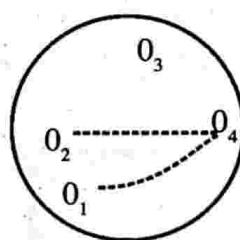


Figure 2.17

Translational symmetry elements

There are two translation symmetry elements exhibited by crystals. They are screw axis and glide planes.

Screw axis

When a rotation corresponding to 2 –, 3 –, 4 – or 6 – fold axis combines with a translation parallel to the rotation axis will give rise to a new symmetry element called the screw axis.

For example within a crystalline structure there are identical atoms a_1 , a_2 , a_3 , a_4 and a_5 as shown in figure below. t is the distance between a_1 and a_3 . This crystalline structure exhibits screw axis. The atom a_1 which is related to a_2 by a rotation

$180^\circ \left(\frac{2\pi}{2} \right)$ followed by $\frac{t}{2}$ parallel to the rotation axis. This element of symmetry is referred to as 2 – fold screw axis and is denoted by 2_1 . The ordinary 2 – fold axis is also shown in figure.

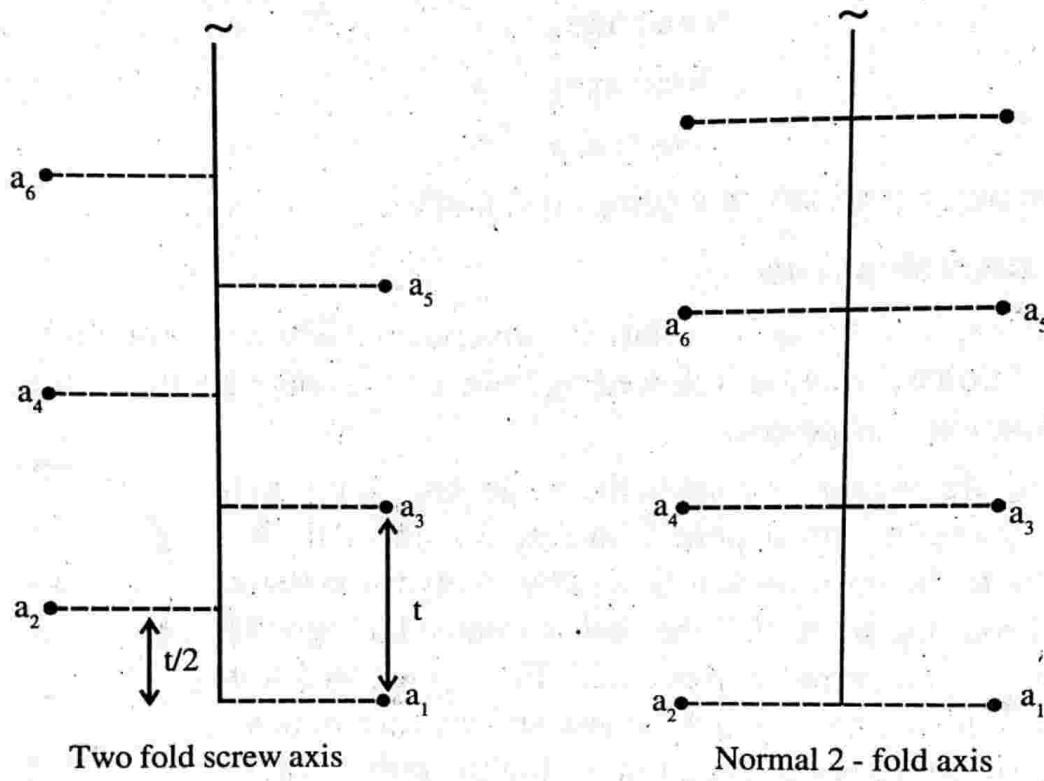


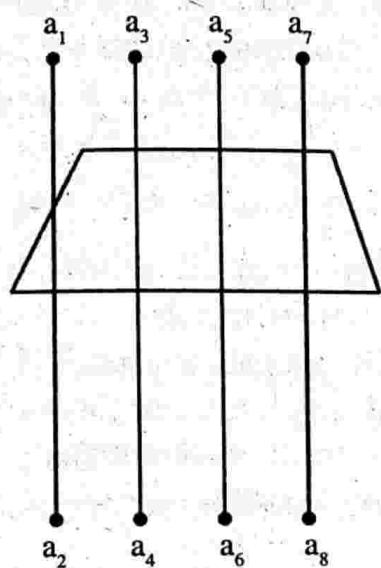
Figure 2.18

Similarly a 3 - fold axis generates 3_1 and 3_2 screw axis. 3_1 corresponds to 120° rotation about the axis followed by a translation $\frac{t}{3}$, 3_2 corresponds 120° rotation plus a translation equal to $\frac{2}{3}t$. Similarly 4_1 , 4_2 , 4_3 are screw axes generated by the 4 – fold axis. The 6 – fold axis generates 6_1 , 6_2 , 6_3 , 6_4 and 6_5 screw axis.

In general a screw axis is represented by the symbol n_m . This is performed by a rotation of $\frac{2\pi}{n}$ and translation of $\frac{m}{n}$ times the translation vector parallel to the rotation axis.

Glide planes

The operation in a glide plane involves a translation $\frac{t}{2}$ parallel to a reflection plane followed by reflection across the plane. t denotes the distance between the successive atoms a_1 and a_3 . Figure shows the glide plane and the ordinary mirror plane.



Normal mirror plane

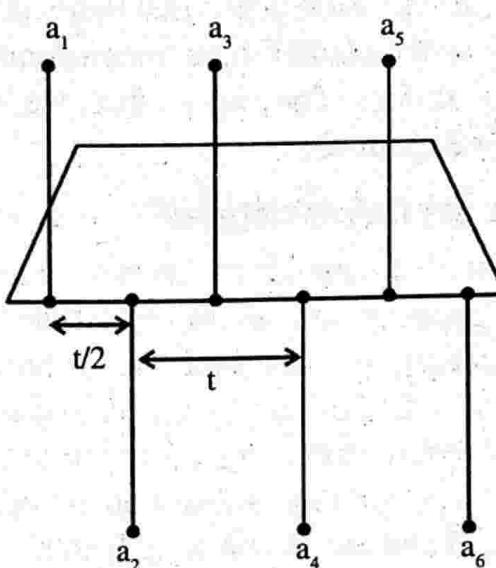
Glide plane with glide component $t/2$

Figure 2.19

Glide planes are divided into three types. They are (i) axial glides (ii) diagonal glides and (iii) diamond glides.

Axial glides are planes whose glide component is parallel to a crystallographic axis a or b or c and equal in length to $\frac{a}{2}$ or $\frac{b}{2}$ or $\frac{c}{2}$. These are symbolised as a glide or b glide or c glide. Diagonal glides have the notation n and they correspond to planes with the vector sum of any two of the vectors $\frac{a}{2}, \frac{b}{2}, \frac{c}{2}$ as the glide component. Diamond glide occurs in the structure of diamond and is denoted by d . This plane has the glide component equal to the vector sum of any two of the following

$$\frac{a}{4}, \frac{b}{4}, \frac{c}{4}.$$

Space groups

When we combine rotation symmetries of the point groups with the translational

symmetry, we obtain a space group symmetry. In this manner one generates large number of space groups, 72 to be exact. In addition to point groups plus translational groups some more combined operations such as screw axis and glide planes come in to picture. Thus one obtains 230 different space groups.

The Bravais space lattices

The internal symmetry of a crystal depends on the arrangement in the space lattice. Bravais has established that there are only 14 ways in which similar points can be arranged in a regular three dimensional order. These 14 arrangements are known as Bravais lattices. They are sc, bcc, fcc, st, bt, so, bco, eco, fco, sm, ecm, st, sr and sh already explained.

Metallic crystal structures

In most of the metals the atoms are arranged in some repeatable pattern indefinitely in space. i.e., metals are crystalline. Most of the common metals exhibit simple crystal structure such as cubic, face centred cubic and hexagonal close packed. Here our aim is to see how atoms are packed in these crystal structures. For this we have to familiar with certain crystal structure terms such as coordination number of second nearest neighbours, nearest neighbour distance, atomic radius number of atoms per unit cell and atomic packing factor.

Coordination number or number of nearest neighbours (N)

It is defined as the number of equidistant neighbour that an atom has in the given structure. It is denoted by N.

Greater the coordination number, the more closely packed up will be the structure.

For SC structure, $N = 6$

For BCC structure, $N = 8$

For FCC structure, $N = 12$

Nearest neighbour distance

The distance between the centres of two nearest neighbouring atoms is called nearest neighbour distance. If r is the radius of the atom, the nearest neighbour distance is $2r$.

For SC structure, $2r = a$

For BCC structure, $2r = \frac{\sqrt{3}}{2}a$

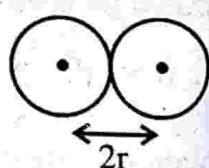


Figure 2.20

For FCC structure, $2r = \frac{a}{\sqrt{2}}$

Number of second nearest neighbours

It is the number of equidistant atoms nearest to first nearest number.

There are 12 second nearest neighbours at distance $\sqrt{2}a$ for SC. There are 6 second nearest neighbours at distance a in BCC. There are 6 second nearest neighbours at distance a in FCC structures.

Atomic radius (r)

It is defined as half the distance between nearest neighbours in a crystal without impurity.

For SC, $r = \frac{a}{2}$, for BCC, $r = \frac{\sqrt{3}}{4}a$ and for FCC, $r = \frac{a}{2\sqrt{2}}$

Number of atoms per unit cell

The number of effective lattice points (atoms) per unit cell is given by

$$n_{\text{eff}} = n_i + \frac{n_f}{2} + \frac{n_c}{8}$$

where n_i is the number of lattice points (atoms) completely inside the cell and n_f and n_c represent the lattice points occupying face centre and corner positions of the cell respectively.

For SC structure:

$$n_i = 0, n_f = 0 \text{ and } n_c = 8$$

$$\therefore n_{\text{eff}} = 1 \times 0 + \frac{1}{2} \times 0 + \frac{1}{8} \times 8 = 1$$

For BCC structure:

$$n_i = 1, n_f = 0 \text{ and } n_c = 8$$

$$\therefore n_{\text{eff}} = 1 \times 1 + \frac{1}{2} \times 0 + \frac{1}{8} \times 8 = 2$$

For FCC structure:

$$n_i = 0, n_f = 6 \text{ and } n_c = 8$$

$$\therefore n_{\text{eff}} = 1 \times 0 + \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 4$$

Atomic packing fraction (APF)

The packing of atoms in a unit cell of the crystal structure of a material is represented by atomic packing fraction (APF).

It is defined as the ratio of volume occupied by the atoms in a unit cell to that of the unit cell.

$$\text{i.e., } APF = \frac{\text{Volume of the atoms per unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{n_{\text{eff}} \times \text{Volume of each atom}}{\text{Volume of the unit cell}}$$

$$APF = \frac{V}{V}$$

Packing factor of simple cubic crystal structure

The simple cubic crystal structure of unit cell consists of atoms located at the corners only (each atom at each corner) and these atoms touch each other along the cube edges. Thus in sc structures we have

$$\text{lattice constant, } a = 2r$$

In sc each atom is surrounded by six equidistant nearest neighbours and hence the coordination number is 6.

Moreover each corner atom is shared by eight unit cells. Hence the share of each corner atom to a unit cell is one-eighth of an atom.

$$\therefore \text{The total number of atoms in effect in one unit cell} = \frac{1}{8} \times 8 = 1$$

In other words the effective number of lattice points in a simple cubic cell is one. Thus sc is a primitive cell.

$$\therefore \text{Volume of all the atoms in a unit cell } V = 1 \times \frac{4}{3} \pi r^3$$

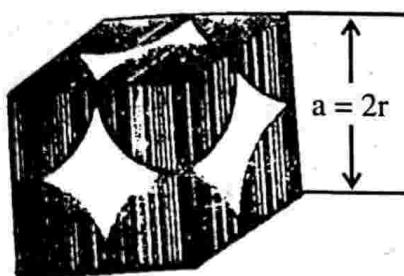
$$\text{Volume of the unit cell, } V = a^3 = (2r)^3$$

$$\therefore \text{The packing factor, } P.F = \frac{V}{V} = \frac{4\pi r^3}{3(2r)^3}$$

$$\text{i.e., } P \cdot F = \frac{\pi}{6} = 0.52 \text{ or } 52\%.$$

Since only half the space of unit cell is filled with atoms, we can say that sc structure is loosely packed structure.

Only one element polonium at a certain temperature exhibits this structure.



Simple cubic structure

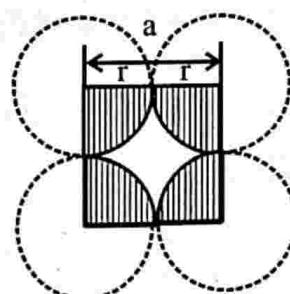


Figure 2.21

Packing factor of body centred cubic structure

In this structure of unit cell there are 8 atoms at the corners and another atom at the body centre. The atoms at the corners do not touch each other but the corner atom touches the body centre along the body diagonal. Hence the coordination number is 8.

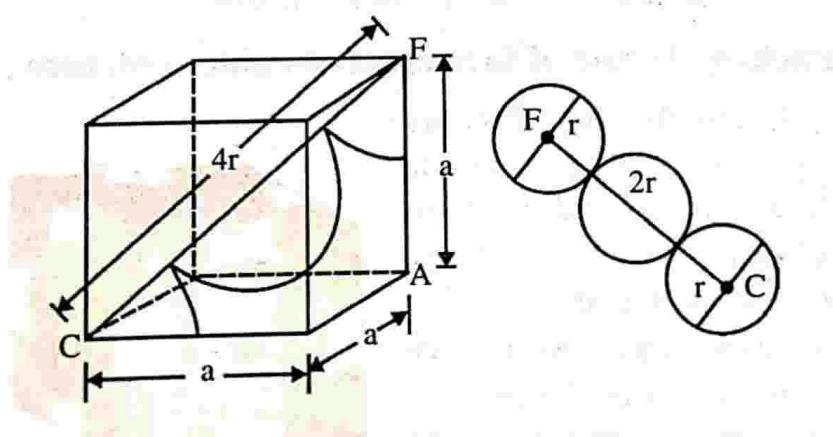
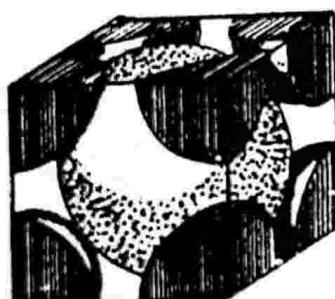


Figure 2.22: Body centred cubic structure

$$\text{The number of atoms in the unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

$$\therefore \text{Volume of the atoms in the unit cell } v = 2 \times \frac{4}{3} \pi r^3$$

$$\text{Volume of the unit cell, } V = a^3$$

$$\therefore \text{Packing factor, } P \cdot F = \frac{V}{V} = \frac{8\pi r^3}{3a^3} \quad \dots\dots (1)$$

From the figure, we have

$$(AC)^2 = a^2 + a^2 = 2a^2$$

$$(FC)^2 = (AC)^2 + (AF)^2$$

$$(FC)^2 = 2a^2 + a^2 = 3a^2$$

$$(4r)^2 = 3a^2$$

$$r = \frac{\sqrt{3}}{4}a$$

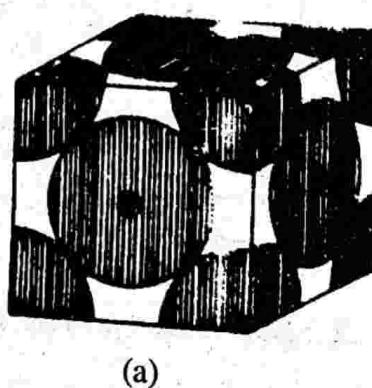
Put this in eqn (1), we get

$$P \cdot F = \frac{8\pi}{3} \frac{\left(\frac{\sqrt{3}}{4}a\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 = 68\%.$$

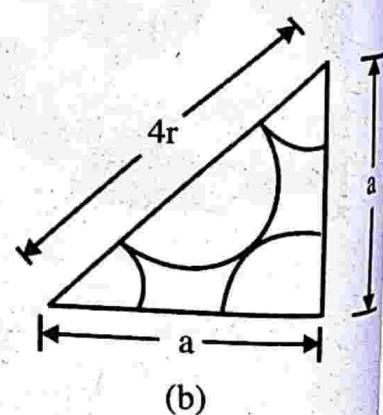
Li, Na, K and Cr exhibit this structure.

Packing factor of face centred cubic structure

In this structure there are eight atoms at eight corners of the unit cell and six atoms at the centres of six faces. The atoms touch each other along the face diagonal. Each corner atom is shared by 8 surrounding unit cells, and each of face centred atom is shared by 2 surrounding unit cells.



(a)



(b)

Figure 2.23: Face centred cubic structure

\therefore The total number of atoms in the unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Volume of all atoms in the unit cell, } v = 4 \times \frac{4}{3} \pi r^3$$

$$\text{Volume of the unit cell, } V = a^3$$

$$\therefore \text{The packing factor, } P.F = \frac{v}{V}$$

$$\text{i.e., } P.F = \frac{16\pi r^3}{3 \times a^3} \quad \dots \dots (1)$$

From the figure we have

$$(4r)^2 = a^2 + a^2 = 2a^2$$

$$\text{or } r = \frac{a}{2\sqrt{2}}$$

Put this in eqn (1), we get

$$P.F = \frac{16\pi \times a^3}{3a^3(2\sqrt{2})^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Copper, aluminium, lead and silver exhibit this structure. This is a close packed structure.

Note: The coordination number of each atom in fcc is 12. When the coordination number of an atom is less than 12, we call it as a loose packed structure.

Packing factor of hexagonal close packed structures (hcp)

The very name hexagonal indicates that hcp structure has the shape of hexagon. The unit cell of this contains one atom at each corner, one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell. The atoms touch each other along the edge of the hexagon. Thus $a = 2r$.

The top layer of the hexagon contains seven atoms. Each corner atom is shared by 6 surrounding hexagonal cells and the centre atom is shared by 2 surrounding cells. The three atoms within the body of the cell are fully contributing to the cell.

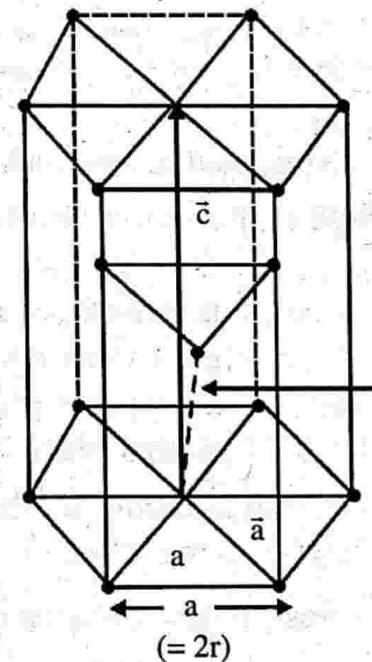


Figure 2.24: Hexagonal close packed structure

Thus the total number of atoms in the unit cell

$$= 6 \times \frac{1}{6} + 6 \times \frac{1}{6} + 1 \times \frac{1}{2} + 1 + \frac{1}{2} + 3 = 6$$

$$\therefore \text{Volume of atoms in the unit cell, } v = 6 \times \frac{4}{3} \pi r^3$$

$$v = \frac{24}{3} \pi \left(\frac{a}{2}\right)^3 = \pi a^3$$

$$\text{Volume of the unit cell (hexagon), } V = \frac{3\sqrt{3}}{2} a^2 c$$

(where c be the height of the unit cell and a be its edge).

$$\therefore \text{Packing factor, } PF = \frac{v}{V} = \frac{\pi a^3}{\frac{3\sqrt{3}}{2} a^2 c} = \frac{2\pi}{3\sqrt{3}} \left(\frac{a}{c}\right)$$

$$\frac{a}{c} \text{ can be evaluated to be } \sqrt{\frac{3}{8}}$$

$$\therefore P \cdot F = \frac{2\pi}{3\sqrt{3}} \frac{\sqrt{3}}{\sqrt{8}} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%.$$

Magnesium, zinc and cadmium exhibit this structure.

Note : (i) In these structures the coordination number is 12. i.e., each atom is surrounded by 12 similar and equal sized neighbours. Out of these 12 neighbours, six lie in one plane, three in an adjacent parallel plane above this plane and three in a similar plane below it.

(ii) Volume of the hexagon = base area \times height = base area $\times c$

Base area = $6 \times$ Area of $\triangle AOB$.

$$= 6 \times \frac{1}{2} AO \times Bd$$

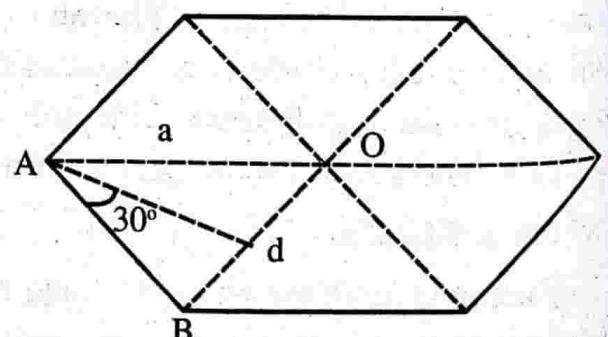


Figure 2.25

$$\text{But } \frac{Ad}{AB} = \cos 30^\circ \therefore Ad = AB \cos 30 = a \frac{\sqrt{3}}{2}$$

$$\text{Base area} = 6 \times \frac{1}{2} \times a \times a \frac{\sqrt{3}}{2} = \frac{3\sqrt{3}}{2} a^2$$

$$\therefore \text{Volume of the hexagon} = \frac{3\sqrt{3}}{2} a^2 c.$$

To evaluate $\frac{a}{c}$

The three body atoms lie in a horizontal plane at $\frac{c}{2}$ from the orthocentres of alternate equilateral triangles.

From the figure

$$AZ^2 = AX^2 + ZX^2$$

$$a^2 = \left(\frac{2}{3} \times \text{median} \right)^2 + \frac{c^2}{4}$$

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4}, \quad a^2 - \frac{a^2}{3} = \frac{c^2}{4}$$

$$\frac{2}{3} a^2 = \frac{c^2}{4}, \quad \frac{a^2}{c^2} = \frac{3}{8}$$

$$\therefore \frac{a}{c} = \sqrt{\frac{3}{8}}$$

Sodium chloride (NaCl) structure

The Bravais lattice of sodium chloride structure is face centred cubic. The basis consists of one Na^+ ion and one Cl^- separated by one half the body diagonal of the unit cube. A unit cell of NaCl comprises four molecules. In this structure each ion is surrounded by six neighbours of the

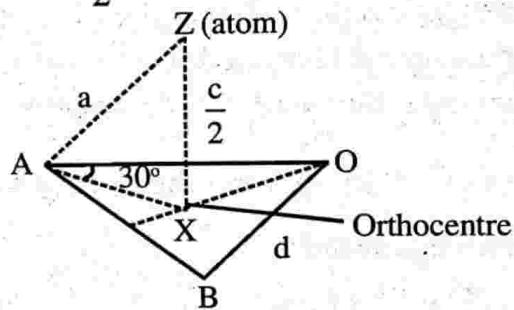


Figure 2.26

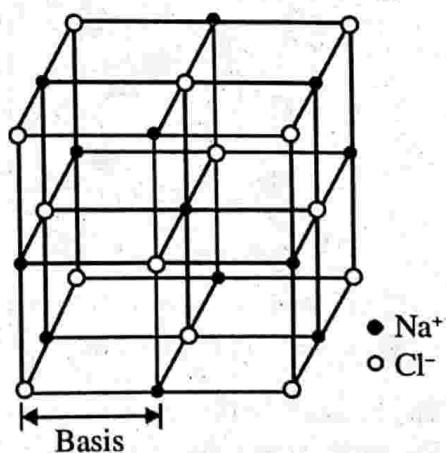


Figure 2.27: Unit cell of sodium chloride structure

opposite kind. Therefore the coordination number is six. The various positions of ions in the unit cell are as follows.

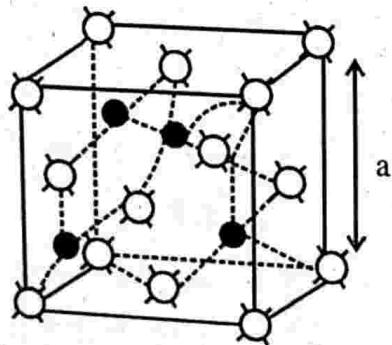
$$\text{Cl}^- : 000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$$

$$\text{Na}^+ : \frac{1}{2}\frac{1}{2}\frac{1}{2}, 00\frac{1}{2}, 0\frac{1}{2}0, \frac{1}{2}00$$

Diamond structure

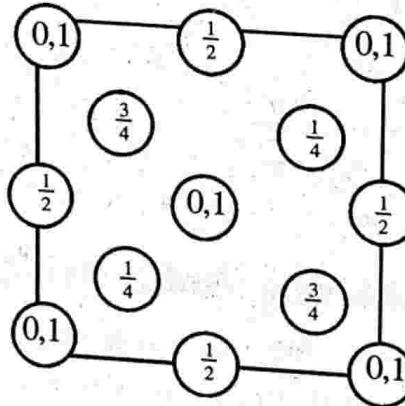
Diamond exhibits both cubic and hexagonal type structures. The diamond cubic (dc) structure is more common and is described here. The Bravais lattice of the diamond cubic structure is fcc with basis consisting of two carbon atoms, one located at the lattice point and other at a distance of one quarter of the body diagonal from the lattice point along the body diagonal. The unit cell of dc structure is shown in figure below. The carbon atoms placed along the body diagonals, in fact, occupy the alternate tetrahedral void positions in the fcc arrangements of carbon atoms. The packing factor of the dc structure is only 34%. The coordination number of each carbon atom is 4 and the nearest neighbour distance is equal to $\sqrt{3} \frac{a}{4}$, where a is the lattice parameter.

The dc structure may also be viewed as an interpenetration of two fcc sub lattices with their origins at $(0, 0, 0)$ and $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$. A plane view of the positions of all the carbon atoms in the unit cell is shown below. The fractional heights of the carbon



○ : C atom occupying fcc position
● : C atom occupying tetrahedral site

The unit cell of dc structure. The lattice is fcc with carbon atoms located at fcc positions and at alternate tetrahedral sites.



Plan view of atomic positions in dc unit cell. Numbers in the circles indicate fractional heights of the carbon atoms.

Figure 2.28

atoms relative to the base of the unit cell are given in the circles drawn at the atomic positions. Two numbers in the same circle indicate two carbon atoms at the same position located one above the other. Other materials exhibiting this type of structure are C, Si, Ge, Gats, Gray tin etc.

Note :

$$\text{From the figure } (XY)^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 = \frac{a^2}{8}.$$

$$XZ^2 = (XY)^2 + (YZ)^2 = \frac{a^2}{8} + \frac{a^2}{16} = \frac{3a^2}{16}$$

$$(2r)^2 = \frac{3a^2}{16}$$

$$\text{or } 2r = \frac{\sqrt{3} a}{4}.$$

$$\therefore \text{Packing factor, } \frac{V}{V} = \frac{8 \times \frac{4}{3} \pi r^3}{a^3} = \frac{\pi \sqrt{3}}{16} = 0.34 \text{ or } 34\%.$$

Zinc sulphide or zinc blende structure

The zinc blende structure is similar to the dc structure except that the two fcc lattices in it are occupied by different atoms and displaced from each other by one quarter of the body diagonal.

The cubic zinc sulphide structure results when zinc atoms are placed on one fcc lattice and 3 atoms on the other fcc lattice as shown. The structure is cubic. There are 4 molecules per unit cell. For each atom, there are four equally distant atoms of opposite kind arranged at regular tetrahedron. CuCl, InSb, CdS etc. exhibit this structure.

The coordinates of Zn atoms are 000,

$0 \frac{1}{2} \frac{1}{2}, \frac{1}{2} 0 \frac{1}{2}, \frac{1}{2} \frac{1}{2} 0$ and the coordinates

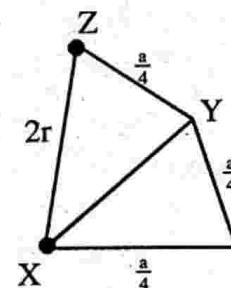


Figure 2.29

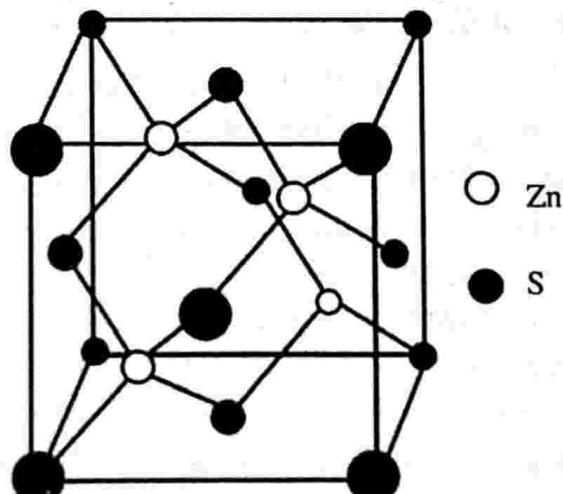


Figure 2.30: Zinc blende structure

of the 3 atoms are $\frac{1}{4} \frac{1}{4} \frac{1}{4}$, $\frac{1}{4} \frac{3}{4} \frac{3}{4}$, $\frac{3}{4} \frac{1}{4} \frac{3}{4}$, $\frac{3}{4} \frac{3}{4} \frac{1}{4}$.

Caesium chloride (CsCl) structure

The Bravais of CsCl is structure is simple cubic. The basis consists of one C_s^+ ion and one Cl^- ion. There is one molecule per primitive cell, with atoms at the corners 000 and body centred positions at the corners $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ of the simple cubic space

lattice. Each ion is at the centre of a cube of ions of the opposite kind, so that the coordination number is 8 obviously, the lattice points of CsCl are two interpenetrating simple cubic lattices, the corner of one sub lattice is the body centre of the other. One sub lattice is occupied by C_s^+ ions and the other by Cl^- ions. CsCl, NH_4Cl , RbCl, TlBr are some materials crystallising in this structure. CsCl structure is shown in figure 2.31.

Finally we give a table of cell properties dc, sc, bcc, fcc and hcp structures

Directions, planes and Miller indices

In a crystal there are large number of atoms situated at the lattice points in different directions and planes. For the study of crystal analysis we have to specify the directions and planes of lattices.

Lattice directions

The direction of line in a lattice is defined by assigning certain indices to this line. For this imagine that the line passes through the origin of the crystallographic axes. Take the coordinate axes of any point on the line. These coordinates are simplified to get a set of the smallest possible integer which when enclosed in a square bracket represents the direction of the lattice.

For example, to determine the lattice direction OQ in a cubic crystal. Take the point

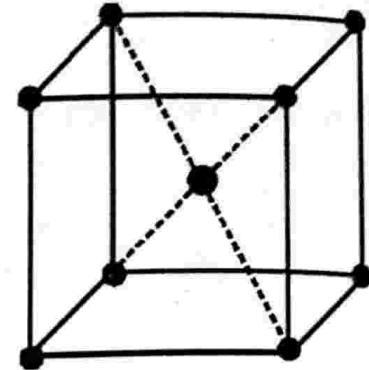


Figure 2.31: Caesium chloride structure

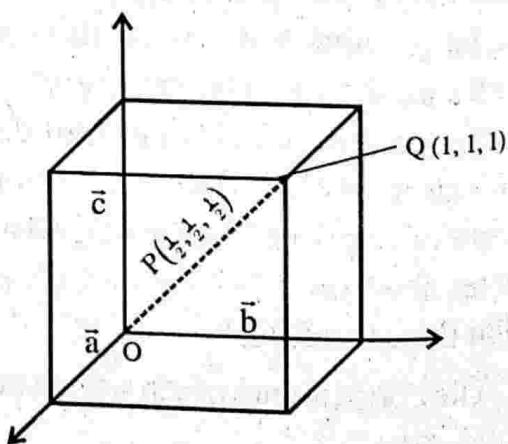


Figure 2.32

Table 2.3 : Cell properties of some crystal structures

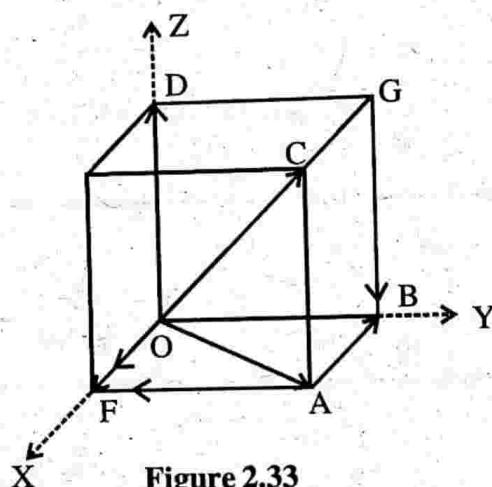
Sl. No.	Properties	Diamond cube (dc)	Simple cube (sc)	Body centred cube (bcc)	Face centred cube (fcc)	Hexagonal close packed structure (hcp)
1.	Volume of unit cell	a^3	a^3	a^3	a^3	$\frac{3}{2}\sqrt{3}a^2c$
2.	Number of atoms per unit cell	8	1	2	4	6
3.	Number of atoms per unit volume	$\frac{8}{a^3}$	$\frac{1}{a^3}$	$\frac{2}{a^3}$	$\frac{4}{a^3}$	$\frac{4}{\sqrt{3}a^2c}$
4.	Number of nearest neighbours (Co-ordination number)	4	6	8	12	12
5.	Nearest neighbour distance ($2r$)	$\frac{a\sqrt{3}}{4}$	a	$\frac{a\sqrt{3}}{2}$	$\frac{a\sqrt{2}}{2}$	a
6.	Atomic radius	$\frac{a\sqrt{3}}{8}$	$\frac{a}{2}$	$\frac{a\sqrt{3}}{4}$	$\frac{a\sqrt{2}}{4}$	$\frac{a}{2}$
7.	Atomic packing factor	$\frac{\pi}{16} = 0.34$	$\frac{\pi}{6} = 0.52$	$\frac{\sqrt{3}\pi}{8} = 0.68$	$\frac{\sqrt{2}\pi}{6} = 0.74$	$\frac{\sqrt{2}\pi}{6} = 0.74$
8.	Examples	Germanium, Silicon and Carbon	Polonium	Sodium, Lithium and Chromium	Aluminium Copper, Silver and Lead	Magnesium, Zinc and Cadmium

$P\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ or $Q(1, 1, 1)$ on this line, either of these points yields the direction as $[1, 1, 1]$.

Remember that any line parallel to $[1, 1, 1]$ lattice direction is represented by $[1, 1, 1]$ since parallel shifting does not change its direction.

It may be noted that the index corresponding to a direction perpendicular to the axis is zero.

It may also be noted that any direction opposite to the direction of crystallographic axis is taken as negative which are putting bars over indices. See the figure below for various examples.



$$\vec{OA} = [1, 1, 0]$$

$$\vec{OB} = [0, 1, 0]$$

$$\vec{OC} = [1, 1, 1]$$

$$\vec{OD} = [0, 0, 1]$$

$$\vec{OF} = [1, 0, 0]$$

$$GD = -(\vec{OB}) = -[0, 1, 0] = [0, \bar{1}, 0]$$

$$GB = -(\vec{OD}) = -[0, 0, 1] = [0, 0, \bar{1}]$$

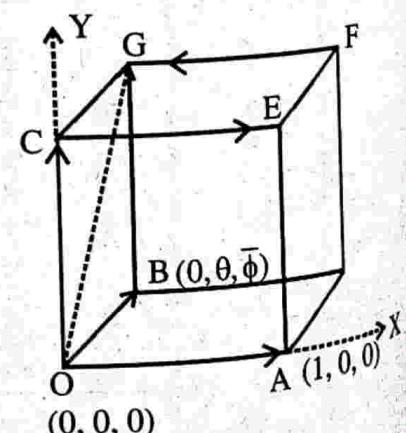
In the figure (33), we have

$$\vec{OA} = [1, 0, 0]$$

$$\vec{OB} = [0, 0, \bar{1}]$$

$$\vec{CE} = [1, 0, 0]$$

$$\vec{FG} = -(\vec{CE}) = -[1, 0, 0] = [\bar{1}, 0, 0]$$



$$\vec{OG} = [0, 1, \bar{1}]$$

$$\vec{AB} = [\bar{1}, 0, \bar{1}]$$

Planes and Miller indices

All crystals are considered to be made up of a set of parallel equidistant planes passing through the lattice points. These planes are known as lattice planes. These lattice planes can be chosen in different ways as shown in figure below.

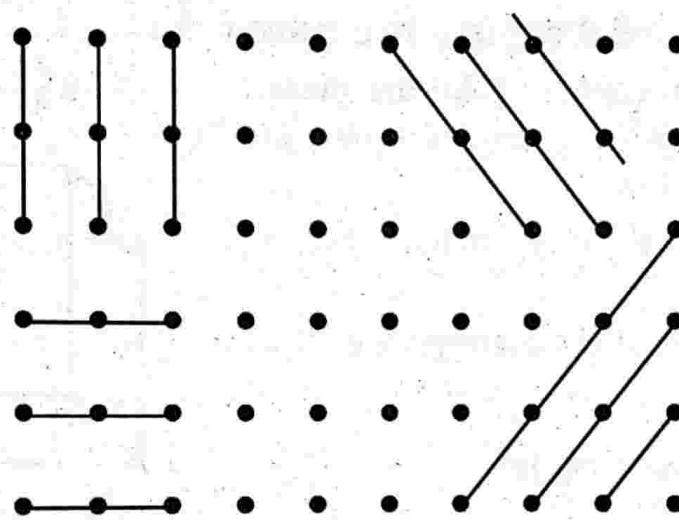


Figure 2.35

The scheme to represent the orientation of planes in a lattice was first introduced by Miller, a British crystallographer.

Miller evolved a method to designate a set of parallel planes in a crystal by three numbers (hkl) known as Miller indices.

Miller indices may be defined as the reciprocals of the intercepts made by the plane on the crystallographic axes when reduced to smallest numbers.

Following are the steps involved in the determination of Miller indices of a plane.

- Find the intercepts of the plane on the crystallographic axes.
- Take reciprocals of these intercepts.
- Simplify to remove fractions, if any, and enclose the numbers obtained into parenthesis ().

In step (i), the intercepts are taken in terms of the lengths of fundamental vectors choosing one of the lattice points as the origin. If a plane is parallel to a certain axis, its intercept with that axis is taken as infinity. In step (ii) the reciprocals are taken in order to avoid the occurrence of infinity in the Miller indices.

Important features of Miller indices of crystal planes

- All the parallel equidistant planes have the same Miller indices. Thus the Miller indices define a set of parallel planes.
- A plane parallel to one of the coordinate axes has an intercept at infinity.
- If the Miller indices of two planes have the same ratio. i.e., $(3, 1, 1)$ and $(6, 2, 2)$, then the planes are parallel to each other.
- If (h, k, l) are the Miller indices of a plane, then the plane cuts the axes into h, k and l equal segments respectively.

Important planes and directions in a cubic crystal

Consider a cubic crystal. Take the plane ABCD (shaded) of the cubic crystal shown in figure 2.36 shown below.

The plane cuts the x-axis at infinity, y-axis at 1, z-axis at ∞ .

\therefore The coordinates of the intercepts are

$$\infty, 1, \infty$$

Taking the reciprocal, we get

$$\frac{1}{\infty}, 1, \frac{1}{\infty}$$

or $0, 1, 0$

Hence $(0 \ 1 \ 0)$ are the Miller indices of the plane ABCD.

Also see that the direction \vec{OC} is given by $[0 \ 1 \ 0]$.

i.e., the plane $(0 \ 1 \ 0)$ is perpendicular to the direction $[0 \ 1 \ 0]$.

The cube faces of a cubic crystal are $(1 \ 0 \ 0)$, $(0 \ 1 \ 0)$, $(0 \ 0 \ 1)$, $(\bar{1} \ 0 \ 0)$, $(0 \ \bar{1} \ 0)$ and $(0 \ 0 \ \bar{1})$.

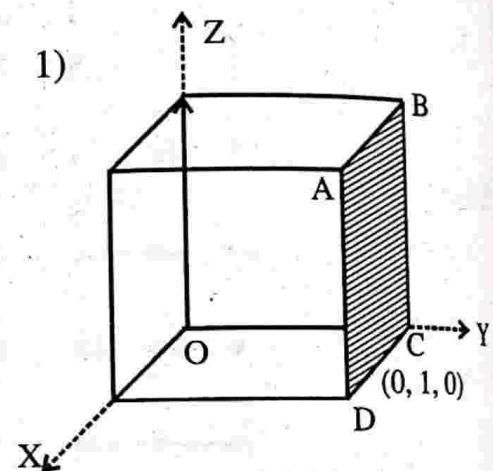


Figure 2.36

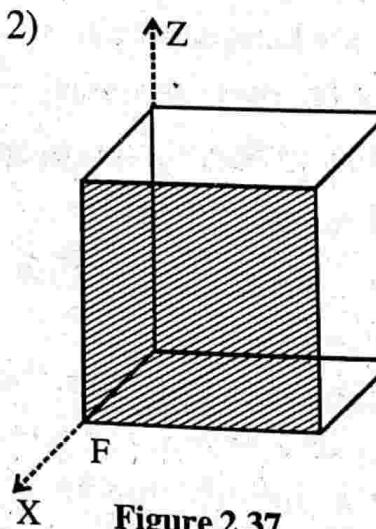


Figure 2.37

$$\text{Intercepts} = 1, \infty, \infty$$

$$\text{Reciprocals} = 1, \frac{1}{\infty}, \frac{1}{\infty}$$

$$\text{Miller indices} = (1 \ 0 \ 0)$$

The direction \overrightarrow{OF} is $[1\ 0\ 0]$

i.e., The plane $(1\ 0\ 0)$ is perpendicular to $[1\ 0\ 0]$ direction.

3)

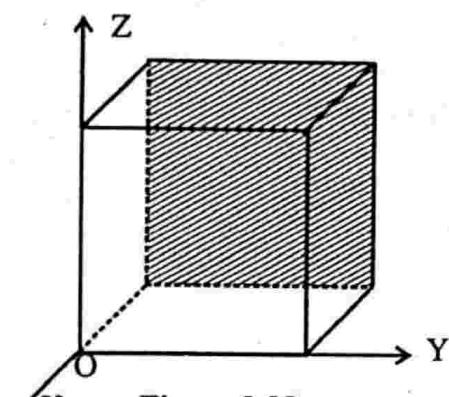


Figure 2.38

The intercepts are $-1, \infty, \infty$

Reciprocals are $\bar{1}, 0, 0$

Miller indices are $(\bar{1}\ 0\ 0)$

Note : If a plane cuts an axis on the negative axis the corresponding index is negative.

4)

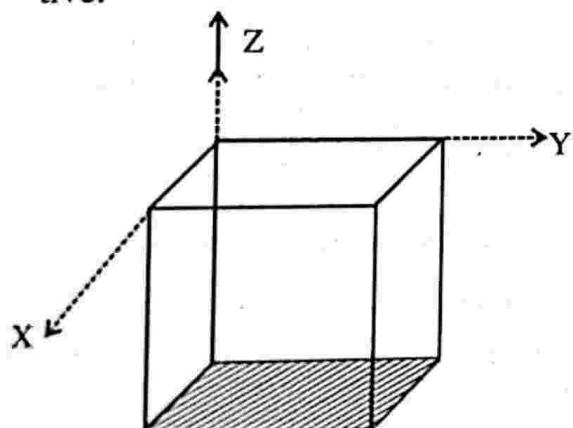


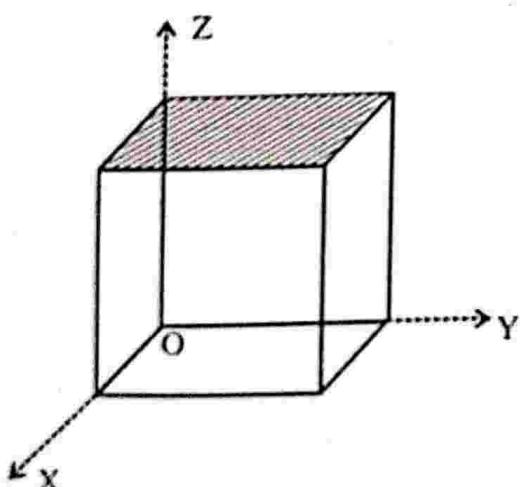
Figure 2.39

The intercepts are $\infty, \infty, -1$

Reciprocals are $0\ 0\ \bar{1}$

Miller indices are $(0\ 0\ \bar{1})$

5)



The intercepts are $\infty, \infty, 1$

Reciprocals are $0, 0, 1$

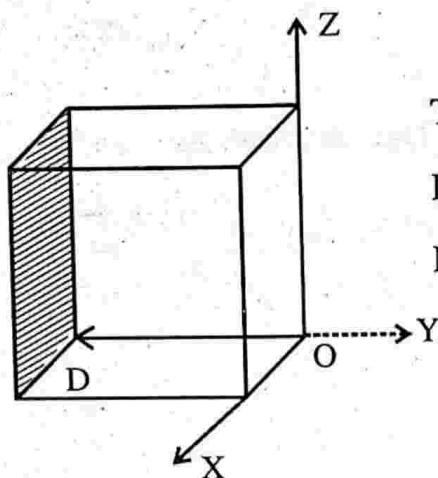
Miller indices are $(0\ 0\ 1)$

Figure 2.40

Direction \overrightarrow{OD} is $[0\ 0\ 1]$

i.e., The plane $(0\ 0\ 1)$ is perpendicular to the direction $[0\ 0\ 1]$.

6)



The intercepts are $\infty, -1, \infty$

Reciprocals are $0, \bar{1}, 0$

Miller indices are $(0\ \bar{1}\ 0)$

Figure 2.41

The direction \overrightarrow{OD} is $[0\ \bar{1}\ 0]$.

i.e., The plane $(0\ \bar{1}\ 0)$ is perpendicular to the direction.

Note : In cubic crystals direction $[h\ k\ l]$ is perpendicular to the plane $(h\ k\ l)$. But in general it is not so.

Distribution of atoms in the atomic planes of a simple cubic crystal

Consider the $(0, 1, 0)$ plane of a simple cubic crystal. See figure 2.35.

Let a be the lattice constant in millimetre and r be the radius of the atom in millimetre.

$a^2 \text{ mm}^2$ contains 1 atom.

$$\therefore 1 \text{ mm}^2 \text{ contains } \frac{1}{a^2} \text{ atoms}$$

But we know that $a = 2r$ (see figure 2.21)

Thus we can say that 1 mm^2 contains $\frac{1}{4r^2}$ atoms. i.e., atoms per $\text{mm}^2 = \frac{1}{4r^2}$

For the plane (110)

See the (110) plane shown below.

Here one side of the plane = a

The other side of the plane = $\sqrt{2}a$

$$\therefore \text{The area of the plane} = a\sqrt{2}a = \sqrt{2}a^2$$

i.e., $\sqrt{2}a^2 \text{ mm}^2$ contains one atom

$$\therefore 1 \text{ mm}^2 \text{ contains } \frac{1}{\sqrt{2}a^2} \text{ atoms}$$

$$\text{Thus } 1 \text{ mm}^2 \text{ contains } \frac{1}{4\sqrt{2}r^2} \text{ atoms}$$

$$(\because a = 2r)$$

$$\therefore \text{Atoms per mm}^2 = \frac{1}{4\sqrt{2}r^2}.$$

For the plane (111)

See the (111) plane shown in figure below. The base of the triangle $= \sqrt{2}a$

$$\text{Altitude of the triangle} = \frac{\sqrt{3}}{2}a$$

$$\therefore \text{Area of the plane} = \frac{1}{2}b \cdot h$$

$$= \frac{1}{2}\sqrt{2}a \cdot \frac{\sqrt{3}}{2}a = \frac{\sqrt{3}a^2}{2}.$$

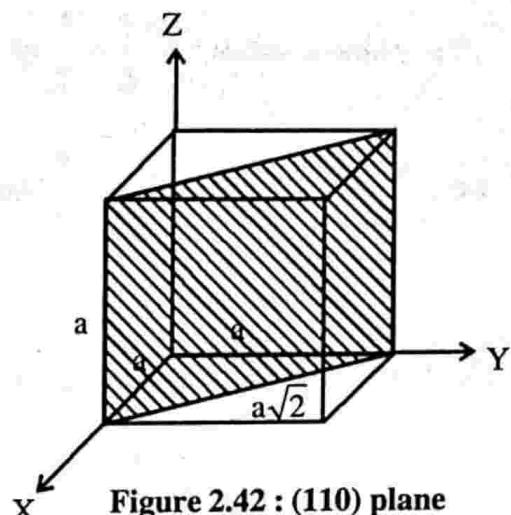


Figure 2.42 : (110) plane

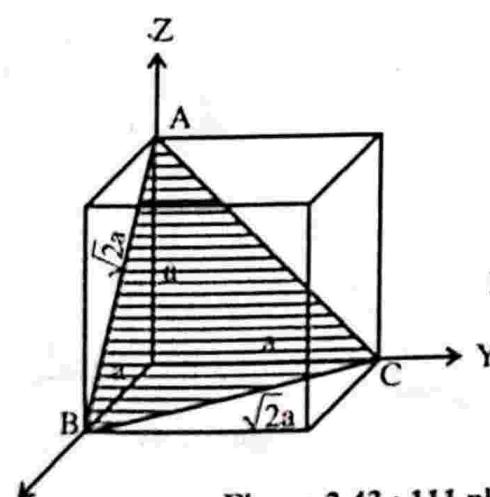
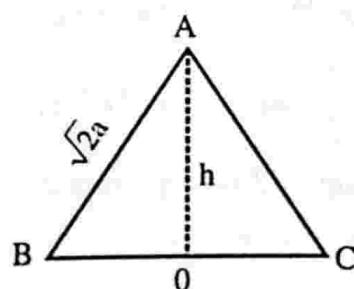


Figure 2.43 : 111 plane



$$BC = \sqrt{2}a$$

$$BO = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$$

$$h^2 = AB^2 - BO^2$$

$$h^2 = (\sqrt{2}a)^2 - \left(\frac{a}{\sqrt{2}}\right)^2 = 2a^2 - \frac{a^2}{2} = \frac{3}{2}a^2$$

$$h = \sqrt{\frac{3}{2}}a$$

This plane contains = $\frac{3}{6} = \frac{1}{2}$ atoms

i.e., $\frac{\sqrt{3}}{2} a^2 \text{ mm}^2$ contains $\frac{1}{2}$ atoms

$$\therefore 1\text{mm}^2 \text{ contains } \frac{\frac{1}{2}}{\frac{\sqrt{3} a^2}{2}} \text{ atoms} \quad \because a = 2r$$

We can say, 1mm^2 contains $\frac{1}{4\sqrt{3}r^2}$ atoms

i.e., Atoms per $\text{mm}^2 = \frac{1}{4\sqrt{3}r^2}$

Similarly we can calculate atom per mm^2 for all the planes.

Separation between lattice planes in a cubic crystal

Expression for interplanar distance

Consider O as the origin and OX, OY, OZ as three rectangular cartesian axes. Let a reference plane pass through O, and consider a set of parallel planes defined by Miller indices (hkl) . Beside reference through O, if next plane passes through A, B and C. Then the

respective intercepts are $\frac{a}{h}$, $\frac{b}{k}$ and $\frac{c}{l}$. If ON is

the normal between this plane and the reference plane, then $ON = d$ is the interplanar spacing.

Let the normal make angles α, β, γ with crystal axes such that

$$\angle NOX = \alpha, \angle NOY = \beta, \text{ and } \angle NOZ = \gamma$$

From the figure we have

$$d = \frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma$$

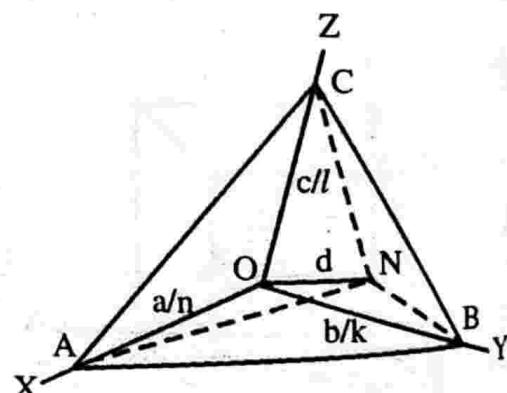


Figure 2.44

or $\cos \alpha = \frac{dh}{a}, \cos \beta = \frac{dk}{b}, \cos \gamma = \frac{dl}{c}$

In a 3D space the direction cosines satisfy the relation.

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

$$\therefore \left(\frac{dh}{a} \right)^2 + \left(\frac{dk}{b} \right)^2 + \left(\frac{dl}{c} \right)^2 = 1$$

$$d^2 \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = 1$$

or $d = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}}$

For a simple cubic lattice $a = b = c$

$$\therefore \text{The interplanar distance, } d = \frac{a}{(h^2 + k^2 + l^2)^{\frac{1}{2}}}$$

This is denoted by d_{hkl}

Thus $d_{100} = \frac{a}{(1^2 + 0^2 + 0^2)^{\frac{1}{2}}} = a$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

Thus $d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$

Similarly for fcc lattice

$$d_{100} = \frac{a}{2}, d_{110} = \frac{a}{2\sqrt{2}} \text{ and } d_{111} = \frac{a}{\sqrt{3}}$$

For bcc lattice $d_{110} = \frac{a}{2}$, $d_{110} = \frac{a}{\sqrt{2}}$ and $d_{111} = \frac{a}{2\sqrt{3}}$

Example 1

Calculate the interplanar spacing for a (321) plane in a simple cubic lattice whose lattice constant is 4.2×10^{-10} m.

Solution

$$a = b = c = 4.2 \times 10^{-10} \text{ m}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For the plane (321), $h = 3$, $k = 2$ and $l = 1$

$$d_{321} = \frac{a}{(3^2 + 2^2 + 1^2)^{\frac{1}{2}}} = \frac{a}{\sqrt{14}}$$

$$d_{321} = \frac{4.2 \times 10^{-10}}{\sqrt{14}} = 1.12 \times 10^{-10} \text{ m}$$

Example 2

In a tetragonal lattice $a = b = 0.25 \text{ nm}$ and $c = 0.18 \text{ nm}$. Deduce the lattice spacing between (111) planes

Solution

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}}$$

Here $h = 1$, $k = 1$, and $l = 1$

$$a = b = 0.25 \text{ nm} \text{ and } c = 0.18 \text{ nm}$$

$$d_{111} = \left[\frac{1}{(0.25)^2} + \frac{1}{(0.25)^2} + \frac{1}{(0.18)^2} \right]^{-\frac{1}{2}} \text{ nm}$$

$$d_{111} = 0.126 \text{ nm}$$

X-Ray diffraction

Introduction

X-rays are electromagnetic waves and they should exhibit the phenomenon of diffraction. However unlike visible, X-rays cannot be diffracted by devices such as ruled diffraction gratings because of their shorter wavelengths (0.1 nm order). In 1921 German physicist Max Von Laue suggested that a crystal which consisted of a 3D array of regularly spaced atoms could serve the purpose of grating. This is possible because all the atoms in a single crystal are regularly arranged with interatomic spacing of the order of a few angstroms and this is compatible with the conditions required to be satisfied for diffraction to take place.

On the suggestion of Laue, his associates, Friedrich and Knipping later successfully demonstrated the diffraction of X-rays from a thin crystal of zinc blende (ZnS). The diffraction pattern obtained on a photographic film consisted of a central spot and a series of dark spots arranged in a definite pattern around the central spot. Such a pattern is called the Laue's pattern and reflects the symmetry of the crystal. After that the phenomenon of X-ray diffraction has become an invaluable tool to determine the structure of crystals. It is also used to determine the wavelengths of X-rays.

Braggs' law

In 1912 W.H. Bragg and W.L. Bragg put forward a model which generates the conditions for diffraction in a simple way. According to their model a crystal is an aggregate of large number of parallel atomic planes. If X-rays are considered to be reflected by such a set of parallel planes followed by the constructive interference of the resulting reflected rays, the diffraction pattern is obtained. Thus the problem of diffraction of X-rays by the atoms converted into the problem of reflection of X-rays by the parallel atomic planes. Based on these considerations, Braggs derived a simple mathematical relationship which is the condition for the reflection to occur. This condition is known as the Braggs' law.

Derivation of Braggs' law

Consider a set of parallel atomic planes with interplanar spacing d . Let a parallel beam of X-rays of wavelength λ be incident on these parallel planes at a glancing angle θ such that the rays lie in the plane of the paper. Consider two such rays 1 and 2 which strike the first two planes and get partially reflected at the same angle θ . The diffraction is the consequence of constructive interference of these reflected rays. Let PL and PM be the perpendiculars drawn from the point P on the incident and reflected portions of ray 2.

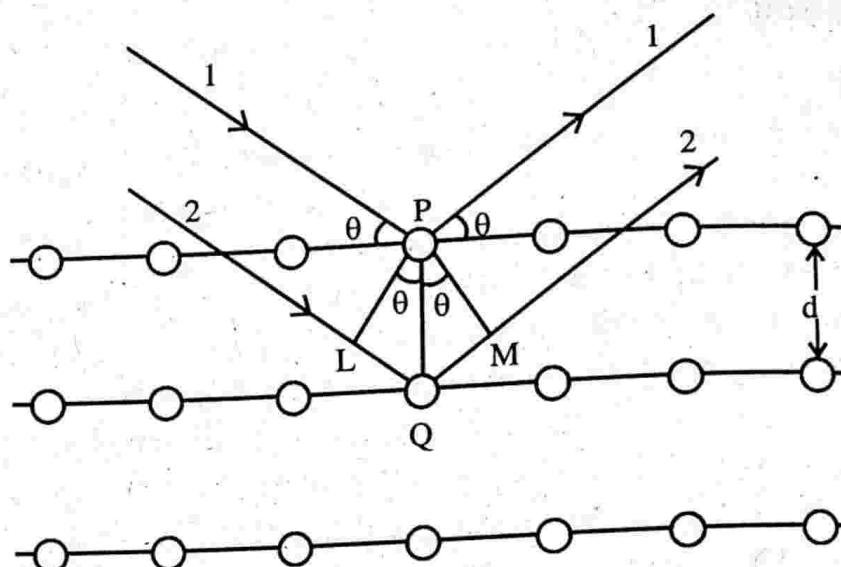


Figure 2.45: Bragg's reflection of x-rays from the atomic planes

The path difference between the rays 1 and 2

$$= LQ + QM$$

From the figure we have

$$\frac{LQ}{PQ} = \sin \theta$$

or

$$LQ = PQ \sin \theta = d \sin \theta$$

and also

$$QM = d \sin \theta.$$

\therefore The path difference = $2d \sin \theta$.

For constructive interference of rays, the path difference must be an integral multiple of wavelength λ .

i.e., $2d \sin \theta = n\lambda$, where n is an integer.

This equation is called Braggs law. For $n = 0$, we get the zeroth order reflection which occurs for $\theta = 0$ i.e., in the direction of incident ray and hence cannot be observed experimentally. The diffractions corresponding to $n = 1, 2, 3, \dots$ etc. are called first, second, third etc. order diffractions.

The highest possible order is determined by the condition that $\sin \theta \leq 1$ and $\lambda \leq d$ for Bragg reflection to occur. Taking $d \approx 10^{-10} \text{ m}$, we get $\lambda \leq 10^{-10} \text{ m}$ or 1 Å° . X-rays having wavelengths in this range are, therefore, preferred for analysis of crystal structures.

Braggs X-ray spectrometer

It is an apparatus devised by Bragg to verify his equation $2d \sin \theta = n\lambda$ and hence to study the crystal structure. It consists of an X-ray tube (coolidge), two slits S_1 and S_2 , a turn table and an ionisation chamber. X-rays from the X-ray tube is allowed to pass through slits S_1 and S_2 so as to obtain a narrow beam which is then allowed to fall on a single crystal (D) mounted on the turn table. The crystal is rotated by means of the turn table to change the glancing angle (θ) at which X-rays are incident at the exposed face of the crystal. The X-rays reflected from the crystal is allowed to enter into an ionisation chamber which is used for measuring the intensities of the reflected rays. Measure the glancing angles θ_1 , θ_2 and θ_3 corresponding to maximum intensities for $n = 1, 2$ and 3 - respectively. From Bragg's equation

$$2 d \sin \theta_1 = \lambda \quad \text{for } n=1$$

$$2 d \sin \theta_2 = 2\lambda \quad \text{for } n=2$$

$$2 d \sin \theta_3 = 3\lambda \quad \text{for } n=3$$

Knowing the glancing angles and λ we can determine the interplanar spacings. This is repeated for different planes.

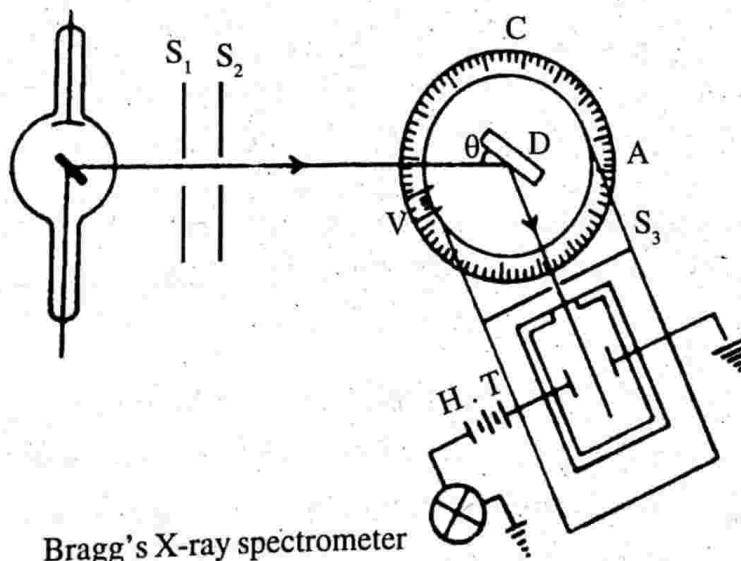


Figure 2.46

The structure of NaCl crystal was studied by using Bragg's spectrometer. The ionisation current was determined for different glancing angles. A graph was plotted between glancing angle and the ionisation current.

It was found from the graph that the first order reflection maxima occurred at 5.9° , 8.4° and 5.2° for $(1\ 0\ 0)$, $(1\ 1\ 0)$ and $(1\ 1\ 1)$ planes respectively.

From Bragg's equation we have

$$2d \sin \theta = n\lambda$$

$$2d \sin \theta = \lambda \text{ for } n = 1$$

i.e., $d \propto \frac{1}{\sin \theta}$

$$d_{100} \propto \frac{1}{\sin 5.9} = 9.73$$

$$d_{110} \propto \frac{1}{\sin 8.4} = 6.85$$

$$d_{111} \propto \frac{1}{\sin 5.2} = 11.04$$

or $d_{100} : d_{110} : d_{111} = 9.73 : 6.85 : 11.04$
 $= 1 : 074 : 1.14$

i.e., $d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

This is nothing but the ratio of interplanar distances in fcc structure. From this Bragg concluded that sodium chloride crystal has a face centred cubic structure.

Rotating crystal method

A single crystal is held in the path of monochromatic radiations and is rotated about an axis. i.e., λ is fixed while θ varies. Different sets of parallel atomic planes are exposed to incident radiations for different values of θ and reflection takes place from those atomic planes for which d and θ satisfy the Bragg's law. This method is known as the rotating crystal method.

In this method a small and well-formed single crystal is mounted perpendicular to the beam. The single crystal having dimensions of the order of 1mm is positioned at the centre of a cylindrical holder concentric with the rotating spindle as shown in figure. A photographic film is attached at the inner circular surface of the cylinder.

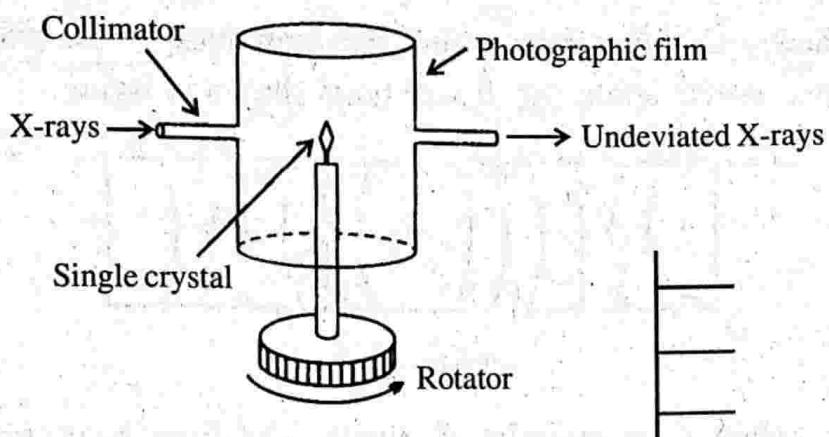


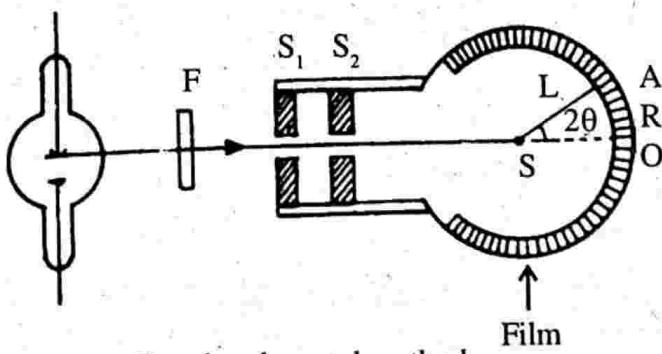
Figure 2.47

The diffraction takes place from those planes which satisfy the Bragg's law for a particular angle of rotation. When the crystal is rotated slowly successive planes pass through orientation, each producing a spot on the film. The position on the film when developed indicates the orientation of the crystal at which spot was formed. The data obtained from these spots give information about the structure of ordinary and complex molecules.

Powder crystal method

The sample in the powdered form is placed in the path of monochromatic X-rays. i.e., λ is fixed while θ and d vary. Thus a number of small crystallites with different orientations are exposed to X-rays. The reflections take place for those values of d , θ and λ which satisfy the Bragg's law. This method is called the powder method. The experimental arrangement consists of a monochromatic X-ray collimated by two slits S_1 and S_2 falls on the powdered specimen taken in a thin glass tube. The specimen S is suspended vertically on the axis of a cylindrical camera. The photographic film is mounted round the inner surface of the camera as shown in figure.

The powder specimen of the crystal can be imagined to be a collection of random oriented tiny crystals exposing all values of glancing angles to the incident beam. For a given λ and a given d , there can be only one value of θ which satisfies Bragg's law. Such reflected beams emerge out from the specimen in all directions inclined at an angle 2θ with the direction of the incident beam. The reflected rays will



Powdered crystal method

Figure 2.48

be on the surface of a cone, vertex at the specimen, base on the photographic film and having semi vertical angle 2θ . It will be as shown in figure.

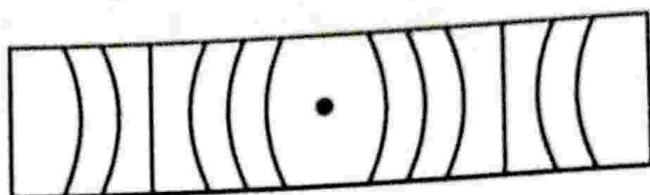


Figure 2.49

Let L be the radius of the cylindrical camera. The direct beam strikes the film at θ . Suppose a spectrum with glancing angle θ is found at A which is at a distance of R from O .

$$\text{Then } \theta = \frac{R}{2L} \left(\text{Angle} = \frac{\text{Arc}}{\text{Radius}} \right)$$

Using this value of θ in Bragg's equation and knowing the value of λ , d the inter planar distance can be calculated. This method is employed in the study of micro crystalline substances like metals, alloys, carbon, fluorescent powders and other forms where single crystals are not available.

IMPORTANT FORMULAE

1. Number of atoms per unit cell, $n_{\text{eff}} = n_i + \frac{n_f}{2} + \frac{n_c}{8}$

$n_i \rightarrow$ number of lattice points

$n_f \rightarrow$ number of lattice points occupying face centre

$n_c \rightarrow$ number of lattice points occupying corners.

2. Atoms packing fraction:

$$\text{APF} = \frac{\text{Volume of atoms per unit cell}}{\text{Volume of the unit cell}}$$

$$\text{APF} = n_{\text{eff}} \times \frac{\text{Volume of each atom}}{\text{Volume of the unit cell}}$$

3. Interplanar distance:

$$d = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}}$$

4. Bragg's law:

$$2d \sin \theta = n\lambda \quad n = 1, 2, 3, \dots$$

5. Properties of crystal structures

Sl. No.	Crystal system (7)	Lattice parameters	Bravais lattice (14)	Examples
1	Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	sc, bcc, and fcc	Ag, Cu, Fe Li, Na, K, Cr, NaCl
2	Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	st, bct	β -Sn, TiO ₂
3	Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	so, bco, eco, fco	KNO ₃ , BaSO ₄ , PbCO ₃
4	Monoclinic	$a \neq b \neq c, \alpha = \beta = 90^\circ \neq \gamma$	sm, ecm	CaSO ₄ · 2H ₂ O, FeSO ₄ , Na ₂ SO ₄
5	Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	st	K ₂ Cr ₂ O ₇ , CuSO ₄ ; 5H ₂ O.
6	Trigonal	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	sr	As, Sb, Bi, Calcite
7	Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	sh	SiO ₂ , Zn, Mg, Cd.

UNIVERSITY MODEL QUESTIONS**Section A****Short answer type questions**

1. What do you mean by solid?
2. What are crystalline and amorphous solids? Give examples.
3. Distinguish between crystalline and amorphous solids.
4. Define (i) a crystal (ii) lattice points and (iii) crystal lattice.
5. How would you generate a crystal structure from a space lattice and a basis?
6. What is a unit cell?
7. Define (i) crystallographic axis (ii) lattice parameters.
8. Distinguish between a primitive cell and a unit cell.
9. What is crystallography?
10. How does a crystal differ from a lattice?
11. Name the seven basic crystal systems.
12. What is a cubic crystal system? What are its Bravais lattices?
13. Draw the unit cells corresponding to sc, bcc and fcc.
14. Define a tetragonal crystal system Draw the unit cells of st and bct.
15. Define (i) point group symmetry and (ii) space group symmetry.
16. What is (i) inversion symmetry
 (ii) reflection symmetry
 (iii) rotation symmetry.
17. When a crystal is said to possess a rotation-inversion axis?
18. Name two translational symmetry elements.
19. What is screw axis symmetry?
20. What is glide plane symmetry?
21. What is meant by coordination number what is its significance?
22. What is atomic packing factor? What does it indicate?
23. Differentiate between loose packed and close packed structures.
24. How do we assign direction to a line in a lattice?
25. What are lattice planes?
26. What are Miller indices? What is their importance?
27. How does hcp structure differ from bcc structure?
28. Explain without calculation, why fcc and hcp structures have the same packing factor.
29. Draw the direction $[1 \bar{1} 1]$ in a cubic crystal.

30. Draw $(\bar{1} \ 1 \ 1)$ plane in a cubic crystal.
31. Draw the following planes of a unit cubic crystal
 (i) $(1 \ 0 \ 0)$ (ii) $(0 \ 1 \ 0)$ (iii) $(0 \ 0 \ 1)$
32. Draw the following planes of a unit cubic crystal
 (i) $(\bar{1} \ 0 \ 0)$ (ii) $(0 \ \bar{1} \ 0)$ (iii) $(0 \ 0 \ \bar{1})$
33. What is the difference between the two planes $(1 \ 0 \ 0)$ and $(2 \ 0 \ 0)$.
34. Draw the $(2 \ 0 \ 0)$ plane of a unit cubic crystal.
35. What type of lattice and basis do the following structures have
 (i) sodium chloride (ii) diamond cubic
36. Write down the various positions of Na^+ and Cl^- in the unit cell of sodium chloride crystal.
37. Write down the coordinates of Zn and S atoms in the unit cell of ZnS .
38. Diamond is the hardest substance known inspite of the fact that the packing factor and the coordination number of carbon atom in the dc structure are quite low. Explain.
39. Write down the various positions of $\text{C} + \text{s}$ and $\text{E}1^-$ in the unit cell of caesium chloride crystal.
40. Draw the unit cell of caesium chloride crystal.
41. What are the important features of Miller indices of a crystal.
42. Draw the following planes of a unit cubic crystal.
 (i) $(1 \ 1 \ 0)$ (ii) $(1 \ 1 \ 1)$
43. Write down an expression for the interplanar distance and explain the symbols used.
44. What is diffraction?
45. Write down Bragg's equation and explain their symbols.
46. Draw the diagram of Bragg's X-ray spectrometer.
47. What are the uses of X-ray diffraction method?
48. Explain why X-ray diffraction method is suitable for the analysis of crystal structures.
49. Why zeroth order diffraction is not considered in X-ray diffraction?
50. Why cannot ordinary optical grating diffract X-rays?

Section B

(Answer questions in about half a page to one page)

Paragraph / problem

1. Derive the packing factor of simple cubic crystal structure.
2. Derive the packing factor of body centred cubic structure.
3. Derive the packing factor of face centred cubic structure.

4. Obtain an expression for the packing fraction for hcp structure.
5. Show that the $\frac{a}{c}$ ratio for an ideal hcp lattice is $\sqrt{\frac{3}{8}}$.
6. Find the Miller indices of one diagonal planes of a unit cubic crystal (1 1 0)
7. Calculate the number of carbon atoms per unit cell of diamond.
8. Show that the packing factor of dc structure is only 34%.
9. Derive an expression for the interplanar distance.
10. Explain the rotating crystal method.
11. Explain the powder crystal method.
12. Derive Bragg's law
13. A plane makes intercepts of 1, 2 and 0.5 Å° on the crystallographic axis of an orthorhombic crystal with $a:b:c = 3:2:1$. Determine the Miller indices of this plane. (312)
14. Obtain the Miller indices of a plane which intercepts $a, \frac{b}{2}, 3c$ in a simple cubic unit cell. (361)
15. The Miller indices of a plane in a simple cubic crystal are 1 2 3. Find the coordinates of the plane $\left(a \frac{b}{2} \frac{c}{3} \right)$
16. Find the Miller indices for planes with intercepts.
 - (i) $a, 2b, \infty$ (ii) $a, b, -c$ (iii) $\frac{a}{2}, b, \infty$ (210, 111, 210)
17. Calculate the distance between two atoms of a basis of the diamond structure. If the lattice constant of the structure is 5 Å° . (2.17 Å°)
18. The Miller indices of a plane is (3 2 6), sketch the plane.
19. A plane makes intercepts of 1, 2 and 3 Å° on the crystallographic axes of an orthorhombic crystal with $a:b:c = 3:2:1$. Determine the Miller indices of this plane (9, 3, 1)
20. The spacing between successive (100) planes in NaCl is 2.82 Å . X-rays incident on the surface of the crystal is found to give rise to first order Bragg reflection at glancing angle 8.8° . Calculate the wavelength of X-rays. (0.863 Å)
21. Calculate the glancing angle on the plane (110) of a cubic rock salt crystal ($a = 2.81\text{ Å}$) corresponding to second order diffraction maxima of wavelength 0.71 Å . (20.934 $^\circ$)
22. The Bragg angle for the first order reflection from (111) plane in a crystal is 60° calculate the interatomic spacing if X-rays of wavelength $1.8 \times 10^{-10}\text{ m}$ are used (1.8 $\times 10^{-10}\text{ m}$)

23. If X-rays of wavelength 0.5 \AA are diffracted at an angle of 5° in the first order. What is the spacing between the adjacent planes of the crystal. At what angle will second maximum occur. ($2.87\text{ \AA}, 10.03^\circ$)
24. A metal with bcc structure shows the first (smallest angle) diffraction peak at a Bragg angle of $\theta = 30^\circ$. The wavelength of X-ray used is 2.1 \AA . Find the volume of the primitive unit cell of the metal. (13.1 \AA^3)
25. The angle of reflection of neutron beam from a crystal of interplanar spacing 3.84 \AA is 30° . Find the speed of the neutron. ($1.03 \times 10^8 \text{ ms}^{-1}$)
26. In a tetragonal lattice $a = b = 0.25\text{ nm}$, $c = 0.18\text{ nm}$, deduce the spacing between (111) planes ($d = 0.126\text{ nm}$)

Section C

(Answer questions in about one or two pages)

Long answer questions - Essays

1. Deduce Bragg's law in X-ray diffraction. Describe Bragg's spectrometer and explain how it is used to determine the wavelength of X-rays.
2. Derive Bragg's law of X-ray diffraction crystals. Give an account of powder method of crystal structure analysis.
3. Derive Bragg's law for X-ray diffraction in crystals. How it is verified. Describe and explain rotating crystal method of crystal structure analysis.

Hints to problems

1. to 12 See book work

13. Intercepts are $1 \frac{1}{2} \frac{1}{2}$

$$\begin{aligned}\text{Intercept in terms of unit cell dimension} &= \frac{1}{a} \frac{2}{b} \frac{1}{2c} \\ &= \frac{1}{3} \frac{2}{2} \frac{1}{2} \\ &= \frac{1}{3} \frac{1}{2} \frac{1}{2} \\ &= 312\end{aligned}$$

Reciprocals

14. Intercepts are $1 \frac{1}{2} \frac{3}{2}$

$$\begin{aligned}&12 \frac{1}{3} \\ &361\end{aligned}$$

Reciprocals

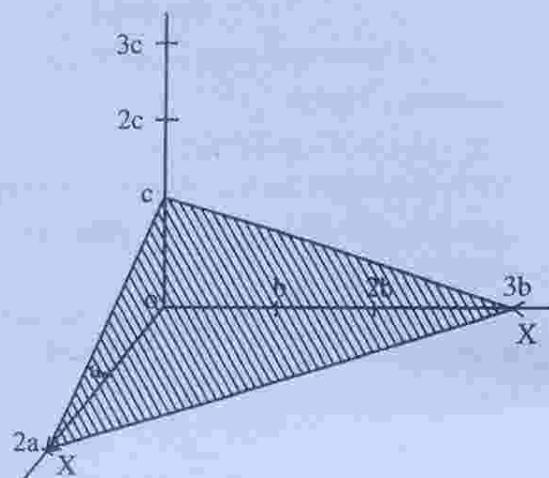
Miller indices

15. Miller indices 1 2 3
 Reciprocals 1 2 3
 \therefore Intercepts $a, \frac{b}{2}, \frac{c}{3}$

16. Try yourself

17. Distance between two atoms in a diamond = $\frac{\sqrt{3} a}{4}$, $a = 5\text{ \AA}^\circ$

18. The coordinates of the Miller indices (3 2 6), are $2a, 3b, c$. Thus the plane is.



19. Same as problem No. 1

20. $2d \sin \theta = n\lambda$

$d = 2.82\text{ \AA}$, $\theta = 8.8^\circ$, $\sin \theta = 0.153$ and $n = 1$ calculate λ .

21. Spacing for (110) plane, $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ $h = 1, k = 1, l = 0 \quad \therefore d = 1.987\text{ \AA}$

Use $2d \sin \theta = n\lambda$, $n = 2$, $\sin \theta = \frac{\lambda}{d} = \frac{0.71 \times 10^{-10}}{1.987 \times 10^{-10}} = 0.3573$

$$\theta = 20.934^\circ$$

22. $2d \sin \theta = n\lambda$, $\theta = 60^\circ$, $\lambda = 1.8 \times 10^{-10}\text{ m}$, $n = 1$

$\therefore d = 1.039 \times 10^{-10}\text{ m}$ gives $d_{111} = 1.039 \times 10^{-10}\text{ m}$,

$$a = d_{111} \times \sqrt{3} = 1.039 \times 10^{-10} \times 1.732 = 1.8 \times 10^{-10}\text{ m}.$$

For a simple cubic $d_{100} = a$ then $d_{111} = \frac{a}{\sqrt{3}}$

23. $2d \sin \theta = n\lambda$. $\lambda = 0.5 \times 10^{-10}$ m, $\theta = 5^\circ$, $\sin \theta = 0.0871$ and $n=1$ we get $d = 2.87 \text{ \AA}$.
For second order maximum

$$2d \sin \theta' = 2\lambda$$

$$\sin \theta' = \frac{\lambda}{d} = \frac{0.5 \times 10^{-10}}{2.87 \times 10^{-10}} = 0.1742$$

$$\theta' = 10.03^\circ.$$

24. $2d_{hkl} \sin \theta = \lambda$

For the first peak $d_{hkl} = d_{110}$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2}} = \frac{a}{\sqrt{2}}$$

$$\therefore a = 2.1 \times \sqrt{2} \text{ \AA}$$

$$\text{Volume of the primitive cell } V = \frac{a^3}{2} = 13.1$$

25. $2d \sin \theta = \lambda$. $\lambda = 2 \times 3.84 \times \sin 30 = 3.84 \text{ \AA}$

$$\lambda = \frac{h}{p} = \frac{h}{mv}, \quad m = 1.67 \times 10^{-27} \text{ kg. Find } v.$$

$$26. d = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}} = \left(\frac{1}{0.25^2} + \frac{1}{0.25^2} + \frac{1}{0.18^2} \right)^{-\frac{1}{2}} \\ = (16 + 16 + 30.86)^{-\frac{1}{2}}$$

$$d = 0.126 \text{ nm.}$$
